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The existence of reversible photosensitivity in some artificial materials containing rutile.

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Introduction.

N 1934 a contribution from America (Parmelee and Badger, p. 2) reported that a certain glaze, containing rutile, showed rapid reverse darkening in daylight. It was stated that C. H. Zwermann, Jr., ibed this photosensitivity to titanium. In the present author's rience the phenomenon is often exhibited, in varying degrees, by mercial glazes based on rutile or on the purified titanium dioxide llable in industry, as well as by glazes made up in the laboratory from nical titanium dioxide of high purity. Lee, also in America, observed rsible darkening in sunlight in commercial titanium dioxide itself, the existence of this effect was confirmed by Williamson (1937) for e brands of commercial titanium dioxide available in Britain. These nds were affected by daylight which had passed through glass, and e tentative suggestions were made regarding the mechanism of the rsible darkening. Later it was demonstrated (Williamson, 1939) reversible darkening in daylight could be produced in a sample of nium dioxide of considerable purity, which was itself not discoloured ight, by contamination with iron according to a special method. sample of titanium dioxide had the following spectrographic ana- (prepared by Messrs. Adam Hilger, Ltd.): Ca, trace; Fe, very slight e; Na, very slight trace, practically nil; P, trace; Pb, minute trace, tically nil; Sb, slight trace; Si, heavy trace; Sn, minute trace.

o o

Elements sought with negative result: Ag, Al, As, B, Ba (probably; lines masked), Be, Bi, Cd, Co, Cr, Cu, K, Li, Mg, Mn, Mo, Ni, Sr, Th, Tl, V, W, Zn, Zr. The same sample has been used throughout the present work. It is also to be understood that any darkening of titanium compounds which may be mentioned occurs in daylight, not direct sunlight, which has passed through glass, and that, unless otherwise stated, the titanium compounds have been confined in such a way that they exhibited the same portions of particle surfaces to the light during the period of illumination (cf. Williamson, 1937).

Three types of photosensitive titanium preparations are subsequently described. They are termed, for convenience, A, B, and C, and consist partly or wholly of rutile. No attempt has been made to obtain a quantitative idea of the photosensitivity, and all three preparations are too fine-grained to show this effect on other than bulk samples.

Type A.

Preparations of Type A were made according to the method already outlined (Williamson, 1939). Titanium dioxide was mixed with an aqueous solution of an appropriate salt of analytical reagent quality, evaporated to dryness, ground, and calcined in a metallic resistance furnace which attained a temperature of 1000° C. at the end of a three hours' cycle. The resulting product was ground, if required, before study, but usually only a feeble suggestion of sintering was to be found.

The most strikingly photosensitive preparations obtained were those of Type A, containing a calculated ratio of 0·2 Fe_2O_3 to 100 TiO_2 in parts by weight, in which the iron had been introduced as ferrous sulphate or ferric ammonium sulphate. These preparations, after storage for some hours in the dark, showed, when, in the form of a heap of powder they were suddenly exposed to the light, a darkening which was so rapid that the eye could easily follow it without reference to any standard for colour comparison. The preparations became obviously darker in a few seconds.

Type A preparations were made also by the use of ferric oxide itself. This was thoroughly ground with the titania and the mixture calcined as usual.

The effect of varying the Fe_2O_3/TiO_2 ratio is indicated in the following table. The iron was added as ferrous sulphate in an amount calculated to give $x Fe_2O_3/100TiO_2$ in parts by weight.

The table indicates that the photosensitivity is not apparent in preparations very low or very high in iron. This may imply a failure in

e mechanism responsible for the colour changes on exposure, but there a strong probability that the failure is, at least in part, in the server's eyes, which cannot detect small colour differences between ry pale, or between very dark, samples.

x.	Unexposed colour.	Exposed colour.
0·05	White	White
0·10	White	Very pale brown
0·20	Nearly white	Pale brown
0·40	Paler medium brown	Darker medium brown
1·00	Strong orange-brown	Strong orange-brown
4·00	Stronger orange-brown	Stronger orange-brown

Microscopic study of the initial titanium dioxide and of the Type A eparations obtained from it revealed little of interest. The titanium oxide grains showed no polarization colours, an effect which is probably be connected with their minute size, but they were detected as tiny rticles, which might show a feeble Brownian movement, at a magni- ation of 2080 diameters. Unground Type A preparations were micro- pically similar, though there was a slight suggestion of sintering gether of grains. Rare ferric oxide particles unconnected with titania peared to exist. No crystalline growth on the surface of titanium xide particles was detected.

Fortunately, through the kindness of Mr. C. C. Paterson, the Research boratories of Messrs. the General Electric Co., Ltd., prepared six X-ray wder photographs of titanium-containing materials. The titanium oxide used throughout the experimental work was revealed as anatase an average crystal size of over 10^{-5} cm. A sample of it, calcined cording to the cycle which was used in making Type A preparations, owed no new crystalline phase and, if there had been any increase in stal size, it was not such as to be revealed by X-ray analysis. The pe A samples, however, exhibited a development of rutile. The results the X-ray studies, which include a very approximate estimate of the ount of rutile present, are shown in the following table:

Metallic salt used.	Ratio $R_2O_3/100TiO_2$ by weight.	Amount of rutile.
. $FeSO_4.7H_2O$	0·2 Fe_2O_3	Not > 15–20 %
. $FeSO_4.7H_2O$	0·4 Fe_2O_3	30 %
. $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	0·2 Fe_2O_3	Not > 5 %
. $MnSO_4.4H_2O$	0·2 Mn_2O_3	Not > 15–20 %

The equilibrium tint of the exposed sample no. 3 was paler than that no. 1. This was perhaps to be correlated with the smaller proportion

of rutile in no. 3. The sample no. 4, containing manganese, was photosensitive also and passed, on exposure to daylight, from greyish-brown to creamy-brown. The colour change was not striking.

Samples made up from ferrous sulphate to give 0·2 $Fe_2O_3/100TiO_2$ but calcined to relatively low temperatures, e.g. from 15° to 615° C. in three hours, were nearly white, with a hint of pink when the powder was in the form of a heap. There was no photosensitivity. This may imply a lack of recrystallization. Ferrous sulphate, calcined by the side of these samples, yielded ferric oxide with traces of undecomposed iron sulphates.

When a Type A sample with 0·2 $Fe_2O_3/100TiO_2$ was held for three hours at temperatures between 1240° and 1250° C. it gave an insensitive material of orange-brown colour, somewhat sintered, with some red-brown spots (iron-oxide?). The microscope indicated recrystallization to anhedral grains, some coarse enough to show polarization colours. The appearance was similar to that of the strongly calcined titanium dioxide itself (vide infra) of which, of course, the present sample largely consisted.

The effects of certain reagents on Type A preparations.

Hot concentrated sulphuric acid effected a slow solution of Type A preparations, but the particles contained in them exhibited, before their complete disappearance, a marked fading of colour. This fading appeared both in preparations low enough in iron to be photosensitive and in those too rich in iron, i.e. too dark, for the sensitivity to be apparent. The fading is not to be attributed to reversible thermosensitivity (vide infra), as the paler colour persisted in the cold sample. It almost certainly results from the solution of an iron-rich portion of the sample and raises problems in connexion with the status of the iron concerned.

Because rutile was produced at the expense of anatase under the conditions prevailing during the calcination of the Type A preparations, it is logical to ascribe the photosensitivity to some type of rutile-iron association. Such an association may involve: (*a*) mechanical mixture of ferric oxide and rutile, where photosensitivity would not be expected to arise; (*b*) adsorption of ferric oxide on rutile surfaces; (*c*) the presence of iron in rutile crystals. There was some microscopic evidence that a small proportion of the iron was present as an oxide merely mechanically mixed in the preparations, but the fact that recrystallization of anatase to rutile has occurred suggests that some iron would be able to enter easily into growing rutile crystals. That photosensitivity appears on

ne entry of impurities into rutile crystals will be apparent from study
subsequent portions of the paper.

There is, however, another point to be considered which concerns the
itile-anatase association. If we postulate the entry of a high proportion
the iron present into the growing rutile crystals, calculation suggests
iat in some cases the crystals might be so dark in colour that, in mega-
opic masses, we should not expect any perceptible photosensitivity.
he very large specific surface, which must exist on the titania which is
e basis of the Type A preparations, implies, however, that we may be
ncerned with a thin rutile film distributed over anatase particles. This
ndition would resemble the metallic oxide-kieselguhr associations
vestigated by Baly, Pepper, and Vernon (pp. 1169, 1172). It is possible
at such a film may exhibit photosensitivity even when megascopic
ystals are too dark to show it.

Type A preparations have been subjected also to attack by a stream
moist hydrogen chloride at temperatures of from 1000° to 1050° C.
olonged treatment removed the iron and with the departure of the
n the photosensitivity disappeared and the preparation became
ite. Concomitantly the crystalline structure of the preparation was
ch modified and the sample became a mass of minute rutile prisms.
however, the treatment was stopped before completion, photosensi-
e rutile crystals resulted (cf. Type C preparations).

Type B.

Type B preparations were obtained by heating titanium dioxide
natase) in molten salt. Various methods have been employed for the
thesis of the crystalline phases of TiO_2, or of substances thought to
them. The methods are summarized by Clarke, Doelter and collabora-
s, and Mellor, and some involve the use of fused salts. The use of
ed sodium chloride does not, however, seem to have been recorded.
e facts that sodium chloride can be obtained as an analytical
gent containing heavy metals only in traces, and that Clews and
ompson effected the conversion of quartz to tridymite in its presence
. 1446–1447), recommended the use of this material in the present
dy.

It was found that sodium chloride readily changed the titanium
xide into new crystalline phases which included rutile. The conver-
n was studied in covered platinum vessels held in various temperature
ges, the lowest being about 860° C. and the highest attaining some
0° C. The resulting titanium compounds showed, in bulk, a slow

darkening in daylight, but were too fine grained for the eye to trace this photosensitivity in individual crystals. There was some variation in the equilibrium tints of unexposed and exposed samples, but in general the change on illumination was from yellowish-white to brown of various shades. Sometimes, however, even the unexposed sample had a brownish tint and this appeared to be more common in preparations made at over 1000° C. The darkening in daylight was usually perceptible after several hours and, if the samples were exposed continuously for some days, tended to become more pronounced, as the reversal during the hours of darkness was slow.

It must be emphasized that the photosensitivity appeared in preparations to which no foreign impurity had deliberately been added. Thus, if the photosensitivity was initiated by the presence of foreign impurities, the sodium chloride or platinum were the most likely source of these. The possibility that platinum itself might promote photosensitivity was tested by making up Type A preparations in which, instead of an aqueous solution of an iron salt, platinum dissolved in aqua regia was used. Grey insensitive powders were obtained. This does not, however, prove the ineffectiveness of platinum in promoting photosensitivity, as recrystallization of the titania may be necessary and it is not known if this has occurred.

If foreign impurities function as promoters of photosensitivity, the presence of this phenomenon in Type B preparations may depend upon the vigorous recrystallization which has occurred. Impurities would easily be picked up by growing crystals and, if well distributed, they may be effective even in minute amount.

More striking photosensitivity was obtainable by the deliberate adulteration of Type B preparations with small quantities of ferric oxide. Alternatively, a sensitive Type A preparation containing iron was recrystallized instead of the usual titanium dioxide, or a certain sample of rutile was used. This rutile sample was one found to confer photosensitivity on glazes.

Sodium chloride melts were heated in electric furnaces, with metallic resistances, but for fusions to be held at low temperatures, e.g. about 860° C., the use of a gas burner was also possible. In the latter circumstance the titanium compounds were found to be very susceptible to even slightly reducing conditions which caused them to acquire a blue tint suggestive of the presence of traces of the ion $Ti^{\cdots}$. If this tint were faint the photosensitivity was not altogether obscured and the preparations darkened to a faint blue-grey on exposure. It may be recalled

at Junker (p. 101) found that carbon monoxide began to react with anium dioxide at as low a temperature as 800° C.

The crystalline phases present in Type B preparations.

Only those preparations made from titanium dioxide and salt, without e addition of iron and other impurities, will be mentioned here. They ve been examined with the polarizing microscope, while Mr. F. A. nnister and Dr. G. F. Claringbull have kindly taken X-ray powder otographs of some of them. In general two phases can be distinguished the microscope, though one phase may be present in too small a antity to be apparent on the powder photograph also.

The insoluble portion of a fusion held for about eleven hours in the nperature range 890° to 910° C. showed, on a powder photograph epared and studied by Mr. Bannister, strong anatase and weak ile lines. With the microscope three constituents were detected . 1):

(*a*) Unconverted grains of the original titanium dioxide which were ubtless responsible for the anatase lines. These had been out of ective contact with the molten sodium chloride and some were still all enough to show a feeble Brownian movement. They were not found subsequent preparations where care was taken to use a large excess sodium chloride and to see that the titanium dioxide was in effective tact with the fused salt, for example by letting it sink in small quanti- s through this material to the bottom of the vessel.

(*b*) Crystals with a refractive index well over that of methylene iodide d with strong birefringence, which formed needles or laths, striated ng their length, without definite terminations. They showed straight nction and negative elongation. Evidence is given later that these not anatase but a sodium titanate.

(*c*) Lozenge-shaped tablets, striated along their length from one acute gle to the other, in which the striations were a direction of straight inction and slow vibration. The edges of the tablets might be tened, parallel to the striations, by the development of crystal faces, d there was sometimes a flat face bisecting the surface of the tablet m which striated planes sloped gently down on either side towards obtuse angles of the lozenge, or towards the edges which appeared tead of these angles (fig. 1). In the absence of any phase which could identified as rutile it was tempting to ascribe these crystals to that ase, the striations being parallel to the *c*-axis. The possibility of an ociation of rutile, not microscopically detectable, with the minute

anatase had also to be considered. The suggestion that the puzzlin crystals were rutile was made more plausible by the existence, in som other fusions, of crystals which, by elongation in the direction of th striations and a loss of tabular habit, appeared transitional to stump rutile prisms.

Fortunately there was no difficulty in discriminating rutile in othe preparations where it was abundant as positively elongated prisms, c varying length, often showing typical twinning, and also as numerou grains less well developed crystallographically (fig. 2). One such pre paration was X-ray photographed by Dr. Claringbull and showed onl the lines of rutile. Indeed, rutile may bulk so largely in some of th preparations that it is difficult to believe that it does not contribute, a least in part, to their photosensitivity. The other constituent, the com pound mentioned under (*b*) above, varies in amount and may be ver important in preparations made at high temperatures. One of these examined by Mr. Bannister, came from a fusion held for six hours a 1145° to 1165° C., and showed lines which were not those of rutile anatase, or brookite. A similar preparation yielded TiO_2 93·16 % an Na_2O 6·76 % on analysis. Preparations made below 1000° C. showed greater though variable TiO_2 content. The unidentified lines in th powder photograph are thus very probably those of a sodium titanate In the presence of titanium dioxide sodium chloride appears to suffer preferential loss of chlorine, which is more pronounced at high tempera tures, with the concomitant formation of sodium titanate. Microscopi evidence does not suggest the formation of more than one sodium titanate The evidence of the powder photograph coupled with the low sod content of the analysed sample may imply the presence of a titanat rich in titania. Otherwise the lines of rutile might be expected on th photograph. The present sodium titanate closely resembles in habit straight extinction, negative elongation, high refractive index an birefringence, and the fact that it is decomposed by hot concentrate sulphuric acid, the compound $Na_2O.3TiO_2$ prepared and analysed b Holmquist (pp. 211–212). The existence of this compound was confirme by Junker. If we assume the presence of the compound in the presen instance, the analysis given may be recalculated as sodium titanat 32·93 % and rutile 66·99 %. This titanate has not yet been isolate from the Type B preparations, but the possibility that it may contribut to their photosensitivity must not be forgotten. It is hoped to invest gate the compound in more detail.

Type C.

These preparations provided direct evidence of the existence of photo-sitivity in rutile, as only this phase has been identified in them under microscope, where it appeared as many tiny prisms, often twinned . 3). Dr. Claringbull kindly X-ray photographed one of the samples d found that the only lines given were those of rutile.

The preparations were obtained by the passage of a stream of moist drogen chloride for some hours over titanium dioxide held at tem-atures between 1000° and 1050° C. The titanium dioxide was con-ned in a glazed porcelain boat, within a silica tube heated by a metallic stance furnace. Chlorine was detected in the gases which issued from tube, as the oxidation of hydrogen chloride, by the air also present the apparatus, was appreciable at the temperatures involved (cf. ws and Thompson, pp. 1443–1444). The titanium dioxide was rystallized to rutile, which was white and showed only a suspicion photosensitivity. Such rutile could then be contaminated by iron, n the resulting pale yellow or pale yellow-brown product was found darken slightly after prolonged exposure to daylight. This contamina-was effected in the same manner as was used for obtaining Type A parations, i.e. the rutile was dried out with a solution of ferrous hate and re-heated. An alternative and better method was to mix initial titanium dioxide with ferric oxide and pass hydrogen chloride the heated product. The iron condensed beyond the furnace, tly as ferric chloride, but, if the reaction were stopped at the right e, the product was converted into rutile crystals containing some rapped iron. This rutile altered slowly in daylight from dirty yellow greyish-yellow. Photosensitive crystals which were grey with a hint rown could also be obtained, apparently because of slight reduction. en such reduction occurred, it could be ascribed to traces of organic ter carried into the furnace from rubber tubing and corks in the aratus for generating and washing the hydrogen chloride. The dition of these parts of the apparatus required careful attention. anium dioxide, with insufficient iron to colour it strongly, became a nite blue through accidental reduction. The work of Junker shows t it is to reduction, and not to thermal dissociation, that the blue ur must be related.

The production of photosensitivity in rutile crystals by permitting n to pick up impurities is reminiscent of the results of an early eriment in recrystallizing titanium dioxide in a stream of gas. Here

a graphite-titania mixture was heated in a current of moist chlorin
It yielded brown photosensitive rutile crystals mixed with ash. But, a
the same time, a sample of titania without graphite was heated on th
down-stream side of the reaction mixture. This became even mo
photosensitive than the rutile crystals just mentioned and passed fro
very pale brown to medium brown on exposure. It contained rutil
and some residual anatase grains, perhaps partly converted to rutile a
in the Type A preparations. Presumably iron, and perhaps other impur
ties, carried from the graphite to the sample, initiated the photosensitiv
effect.

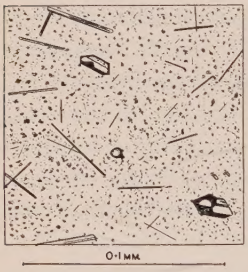

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 1. Titanium dioxide recrystallized in the presence of molten salt. Mar
minute grains of unconverted titanium dioxide (anatase), elongated crystals
sodium titanate, and two crystals presumed to be rutile (towards top left and botto
right corners of square respectively).

FIG. 2. Titanium dioxide recrystallized in the presence of molten salt. Mar
elongated crystals of sodium titanate. The largest crystal in the figure, below t
centre of the diagram, is also this material. Rutile forms short prisms, sometim
twinned, and anhedral grains.

FIG. 3. Titanium dioxide recrystallized, mixed with ferric oxide, in a stream
moist hydrogen chloride. Photosensitive rutile crystals, often twinned.

Reversible thermosensitivity in initial titanium dioxide (anatase) and in Type A preparations.

Lee (pp. 771–772) cites a number of compounds which exhibit reve
sible thermosensitivity, viz. HgI_2, the chromates $RCrO_4$ where R is a
alkaline earth metal, and the mineral gillespite ($FeO.BaO.4SiO_2$). H
points out that the mechanisms of the phenomena involved in reversib
photosensitivity and in reversible thermosensitivity may well ha
common factors.

Reversible thermosensitivity is more familiarly shown by a numb

ommon metallic oxides both coloured and white, e.g. HgO, PbO, SnO_2, and TiO_2. There is remarkably little information available erning the mechanism of this physical change in oxides.

e titanium dioxide (anatase) used as the basis for the present experi- s itself showed gradual and reversible colour changes on heating. nature of these changes is indicated in the following scheme in h are listed the approximate temperatures at which particular rs prevailed:

Room-temperature ...	white.
100° C....	white.
250°	faint brown.
400°	faint brown with tinge of green.
450°	browny-green.
600°	deep yellow-green with hint of brown.

was true of the titanium dioxide used by Junker (p. 98), an ersible darkening occurred at high temperatures. In the present nce this was connected with some type of recrystallization. After held for three hours in the temperature range 1240° to 1250° C. itania became slightly sintered and developed a strong greyish- w colour. Where exposed to air, the surface of the sample had a ver tint. The microscope indicated the presence of grains large gh to show polarization colours. The nature of the change on heat- as not further investigated. The colour produced may be conse- upon alterations in grain-size, or perhaps the production of a new , e.g. rutile, in which foreign impurities can exert a more powerful rial effect than they did in the original anatase. Strongly calcined ium dioxide was still capable of being transformed into a photo- tive preparation of Type A.

ating of the titanium dioxide for two hours at temperatures of to 1110° C. was sufficient for the production of a greyish powder ining small coherent masses. Individual grains in the powder were mall to show polarization colours.

ere was a suspicion, which could not be confidently asserted, that gly calcined titania developed a slight photosensitivity. If this e confirmed, it is possible that the formation of rutile, containing rities residual from the anatase, is involved.

onounced thermosensitivity was shown by the Type A preparations ining 0·2 Fe_2O_3/100TiO_2 and, because of the rapidity of the change lumination, a connexion, real or apparent, with photosensitivity asily established.

o samples were heated in parallel, one exposed to light, and one

shielded from it. The latter could be uncovered at any instant a immediately covered again. A third exposed sample was kept at roo temperature as a check. Initially there was a strong contrast betwe the two samples, the exposed and the unexposed, but at 35° C. difference was less pronounced and the heated exposed sample was pa than the sample kept at room-temperature. At 70° C. no differe could be detected between the exposed and covered heated sampl The difference reappeared on cooling.

The pale brown colour which was found in the heated sample persis to high temperatures, but at 400° C. a strong brownish-green had beco apparent.

After the exposure of samples behind red and violet filters, the sam behind the violet filter had the darker colour, i.e. the red light, like he effected a reversal of colour. In a qualitative though not a quantitat way this observation illustrates Lee's comment on the effect of heat solarized glasses (p. 772) '. . . the colors excited by short wave ul violet light were reversed by long wave radiation (heat)'.

Remarks by Smits, given in his earlier (1922) but not in his later bo (1938), may be worth recalling. He states that some substances, incl ing the so-called phototropic materials, are sensitive to foreign ener The application of such energy, light in the present instance, leads to end state at ordinary temperatures corresponding to a purely therm equilibrium at another temperature (p. 178). The apparently analog condition of the red-illuminated and heated Type A preparations m illustrate this thesis, though it is well to remember that Smits proba had in mind certain types of change in irradiated phototropic materi which may not be valid in the case of rutile.

General Discussion.

The photosensitivity of rutile resembles, sometimes strikingly, so times only remotely, a number of other phenomena. There is, instance, an obvious connexion with the reversible darkening in dayli shown by some brands of commercial titanium dioxide. Such materi are likely to contain rutile (Morgan and Pratt, p. 152). The quant of impurities in them is probably small, yet if these impurities are w distributed photosensitivity might be initiated. Recently the author h seen this sensitivity in a titanium dioxide, not of commercial, but laboratory reagent quality, which passed on exposure to daylight fr a creamy colour to pale brown. The photosensitivity of rutile has a associations with that of glazes containing titanium. It is hoped

ss these associations in a paper in the 'Transactions of the British
nic Society'. More remotely, there is a parallel in certain zircons
ı show rapid colour changes, slowly reversible, in sunlight (Spencer,
2, 189).

ny compounds, both organic and inorganic, suffer colour changes
exposed to radiation of various kinds. The inorganic compounds
le artificial substances and natural minerals. Among the latter,
of historical interest to note, rutile was considered by Doelter
, p. 314) to owe its colour, probably, to radioactive materials.
organic compounds change colour on exposure to light of certain
lengths, and the new colour is reversed when the compound is
l in the dark, or, better, exposed to light of certain other wave-
ıs. Such compounds are said to be phototropic. Various explana-
of this phototropy have been suggested. They are listed by de
k and Le Fèvre (p. 1458), who have themselves elucidated the
anism of the phototropy of certain anils. Under the heading of
tropy the 'International critical tables' (vol. 7, p. 167) cite four
nic compounds and one inorganic mixture, viz. CaS, SrS, Li_2NH,
and lithopone, so it may not be inappropriate to apply the term
tropy to the present reversible photosensitivity, especially as there
e evidence that one part of the spectrum (long waves) may reverse
lour developed by another (short waves). A striking example of
tropy in an inorganic compound was recently recorded by Hibben.
large MgO crystals became deep purple in ultra-violet light. They
rized spontaneously when removed from the light source, but
also be decolorized by certain antagonistic mercury lines. Heating
d up the reversal of the purple colour (cf. Type A preparations).
s suggested that the phenomena are produced by some kind of
n migration connected with impurities in the MgO lattice.

colour changes shown by many minerals, when exposed to heat
iation, have been ascribed to the presence of colloidal impurities,
ample by Doelter, a useful summary of whose work and opinions
en by Lee (pp. 772–773). The flocculation and deflocculation of
olloidal aggregates, which have diameters comparable to the wave-
of light, can provide a mechanism for the colour changes. For
ce, Ekstein recently demonstrated the existence of colloidal
les in artificial crystals of salt, which particles diffused a colour
ding on their size, by the use of the ultra-microscope and a mono-
ator (p. 242). Also, Friend and Allchin have lately shown the
ce of gold (probably colloidal) in celestine. Red celestine contained

more gold than blue, and this more gold than the colourless miner
Heating of the blue mineral turned it slightly pink.

Alteration in the degree of dispersion of colloidal impurities may
responsible for the photosensitivity of rutile, though some type of el
tron migration may be considered as an alternative. Indeed, the t
conceptions are not necessarily incompatible, for, if the conditio
obtaining in hydrosols are even remotely analogous to those existi
where the dispersion medium is a solid, alteration in the charge
colloidal aggregates may be responsible for changes involving floccu
tion or deflocculation.

The development of colour in an irradiated crystal is not necessar
dependent on the presence of foreign impurities, i.e. impurities forei
in the sense that they have no part in the ideal chemical formula for t
material. For instance, in alkali halides, the development of colour h
been ascribed to the trapping of electrons at vacant lattice points, or
the presence of a stoicheiometric excess of alkali metal. Further deta
may be found in an article by Mott. In the case of rutile, however, t
coloration on illumination is much enhanced, and very probab
initiated, by the presence of foreign impurities, including iron a
manganese. Uncontaminated rutile showed only an unconfirmed s
picion of phototropy.

Of much interest in the present study are the investigations
Goodeve and co-workers of the photosensitizing activity of titani
dioxide. Goodeve (1937, p. 340) has shown that this oxide is activa
by the light from a mercury arc which has been filtered through gla
Further, titanium dioxide absorbs light in the near ultra-violet wh
is exactly the region where it is photoactive. The titanium diox
studied by Goodeve probably contained at least a proportion of rut
while that used by Goodeve and Kitchener (1938 a) to effect the pho
sensitized bleaching of 'chlorazol sky blue FF' was almost certai
rutile. It was prepared by the hydrolysis of $TiCl_4$ which Weiser a
Milligan found to yield rutile. These workers indicated, however, t
titanium dioxide obtained by some processes is anatase; so it is
surprising to find that the titania used as a basis for the experime
of the present author was this phase. The possible mechanisms invol
in photosensitization by solids are discussed by Goodeve and Kitche
(1938 b), and it must be borne in mind that there may be a real c
nexion between the photosensitizing activity of titanium dioxide a
the reversible photosensitivity of rutile. In the one case energy is ta
up on irradiation and made capable of effecting chemical change

ıbouring molecular species, while in the other it is absorbed and
ıotes some change, which cannot be certainly specified as yet,
ın the crystal structure which results in an alteration in colour. It
o feasible that the part of the spectrum most effective in causing
larkening of rutile is that which promotes the photosensitizing
ity of titania, viz. the near ultra-violet.

nally, it must be stated that the possible existence of photosensi-
y in anatase and brookite has not been investigated, but the occur-
of this phenomenon in rutile may be worthy of more study by
rch workers. Further, because of the extensive use of titanium
de in industry, their work might well have results extending beyond
ield of pure science.

ctotropy may be found eventually in natural rutile, but most
als are probably too dark for the effect to be detected. In the case
nall detrital rutiles the author's experience suggests that photo-
tivity, even if present, would not be perceived except in a concen-
containing many grains.

Summary.

versible darkening in daylight has been detected in three types of
cial material containing rutile:

Anatase partly recrystallized by heat-treatment, under 'dry'
tions in the presence of iron or manganese, with the production
ile. Certain iron-containing samples show a strikingly rapid darken-
n daylight. This darkening is more pronounced in violet than in
ght and is reversed on heating to below 100° C.

Anatase completely recrystallized in the presence of molten
m chloride. The resulting product contains rutile and a sodium
ate in varying proportions.

Anatase converted into rutile by heating, in the presence of iron,
atmosphere containing hydrogen chloride.

e photosensitivity is held to depend on the entry of impurities into
utile crystals. Tentative explanations of it are given and the pos-
ty of a connexion with the known photosensitizing activity of
ium dioxide is stressed.

is a pleasure to acknowledge the kindness of Mr. F. A. Bannister,
, Dr. G. F. Claringbull, B.Sc., and Mr. C. C. Paterson, O.B.E.,
E.E., M.Inst.C.E., F.Inst.P., in providing X-ray powder photo-
ns. Their contributions have been mentioned in the appropriate
s in the paper and have been of much assistance in the present study.

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new method for the preparation of thin sections of clays.

By A. V. Weatherhead.

Geological Department, King's College, University of London.

[Read January 25, 1940; communicated by Dr. G. F. Claringbull.]

HIN sections of clays are not easily prepared by the routine petrographic methods. The chief difficulties are due to the extremely texture of the clays and to the soft and plastic nature of these erials. These difficulties are only too well known, and, although in e cases they have been partially overcome by impregnation *in vacuo*, safe to assume that really little work has been accomplished in the oscopic examination of clays on account of the difficulty of pro- g satisfactory thin sections. The writer has attempted to extend scope of the microscopic investigation of clay rocks by means of the nique outlined below.

he method has been devised in response to an appeal by a friend, working in a laboratory at a well-known pottery works and thus ected with the clay industry, desired a method that would make ble the examination of thin sections of clays under high powers polarized light. The writer claims that this has been achieved, and method permits the use of oil-immersion objectives at a magnifica- of 1000 or more. It will be seen below that a number of clays nd to this method, with one notable exception. Fuller's earth has resisted attempts in the production of a useful preparation.

echnique.—This method of preparing thin sections of clays is a ification of the principles used for preparing cellulose 'peels' of l plants. These petrifications, which may be either calcareous or ous, are cut in a rock-slitting machine, and after the cut surface been smoothed on the fine grinding plate, it is then etched with ochloric or hydrofluoric acid, whichever the case may be. When he etched surface is covered with pyroxylin, and the latter, when ened by evaporation of the amyl acetate, can be pulled off as a film. his principle is employed for the treatment of clays, with the excep- that no etching with an acid is necessary, for it is essential that lays should be in a perfectly dry condition.

Preparing the specimen.—The clay sample must be prepared and smoothed surface obtained to receive the pyroxylin. Obviously th routine method of wet grinding is impracticable, as the clay will imme diately become plastic. Abrasive powders cannot be used, as coars carborundum tears the surface of the specimen, and the fine powde inevitably lead to contamination.

To obtain the prepared surface, therefore, the clay must be groun on dry glass plates without the use of abrasives. These grinding plate (a convenient size is 12 inches square) are prepared by grinding wit coarse (90), medium (220), and fine (600) grades of carborundum powder and when thoroughly washed and dried they are ready for use. Th coarse plate may be used for rapid smoothing, but the medium and fin plates must be used for obtaining the finished surface: the selection o the finishing plate is determined by the nature of the clay under treat ment as explained below. Preliminary paring can often be achieve with a sharp razor blade. If the clay is extremely fine textured, th best result is obtained by finishing on the medium plate; in other case the fine plate yields a suitable finish.

The grinding operation, carried out by a circular motion with litt or moderate pressure, is begun at the centre of the plate and graduall carried outwards towards the sides, so that as the roughened surfac of the plate is gradually choked up with clay powder, fresh areas ar progressively used. The specimen must be carefully brushed befo proceeding from the coarse to the fine plate. If necessary an addition 'polish' can be obtained by gently rubbing the specimen on a piece good quality glazed notepaper, taking care to brush well afterward The plates must be thoroughly washed when one sample is finished an before commencing on another.

When the grinding operation is completed, the specimen is arrange on a pedestal of plasticine to ensure that the prepared surface is leve it is then ready to receive the pyroxylin.

The pyroxylin as used for the treatment of fossil plants is a very thic viscous solution, but when used for clay rocks it is necessary to dilute in equal proportions with amyl acetate, since it must be borne in mi that a very thin peel is desirable for examination under high-pow objectives. Before applying the pyroxylin the surface of the clay flooded with amyl acetate: a length of glass tubing drawn out to a sma aperture will enable the requisite amount of amyl acetate to be applie The amyl acetate is soon absorbed by the clay and then a small quantit of pyroxylin is spread over the specimen by means of a glass rod. Whe

e pyroxylin has spread evenly over the surface any air bubbles are cked with a mounted needle, but care must be taken to avoid touching e now softened surface of the clay. The preparation is left for about e or six hours to dry, and by supporting a funnel over the specimen st is prevented from settling down into the pyroxylin.

When dry the film is ready to be pulled off: to start the peel the point a penknife is carefully inserted at the edge and carried along a short y, when the whole film can be gradually lifted away from the specimen. on inspection the film appears a little too thick, the clay side of the n may be smoothed down on paper, but with practice this may not ays be necessary.

Mounting the film.—The clay film has now to be mounted, and some ficulty may arise owing to the tendency for the film to curl with the y side inwards, which increases when heated on the mounting plate. prevent this it is placed upon the plate with the clay side downwards held down with a heavy lead weight some $2 \times 2 \times 1$ inches in size. t has been found that temperature control while cooking the balsam ne only way of making a successful and lasting mount of these films. h control is obtained by the attachment of a thermometer to the nting plate. The writer uses a copper plate $8 \times 5 \times \frac{3}{10}$ inches in size pported on a tripod. At one corner of the plate a brass cylinder is d. A well-fitting cork is bored to take a thermometer reading to ° C. the stem of which is wrapped in a piece of copper foil 2 inches and 1 inch wide. When the cork is fitted to the cylinder the bulb he thermometer rests in a cup that has been drilled into the plate to ive it, which ensures good contact between the thermometer and copper plate; the copper foil is adjusted so that it rests directly on plate. The plate is heated by means of a bunsen burner which has a ass attachment and this is adjusted to keep the plate at a constant perature of 45°, at which temperature the mounting of each film is mmenced. To regulate the heating of the plate a screw-clip is fitted ne rubber tubing of the burner and is adjusted so that the tempera- will gradually rise to 120° in 15 minutes. In this way a convenient perature range is obtained and full control over the whole mounting ess is possible.

nada balsam is the mountant used, and for manipulating the clay and cover slips, broad pointed forceps are an advantage; for adjust- nd pressing down the cover glass a match stick, trimmed to a chisel , will be very useful and minimizes the danger of breaking the cover at the critical moment in the mounting process.

Procedure.—The clay film is first trimmed with scissors and placed, *clay side down*, on the mounting plate, which is at 45°, and pressed down with the lead weight for 15 minutes, or longer if possible, to ensure that

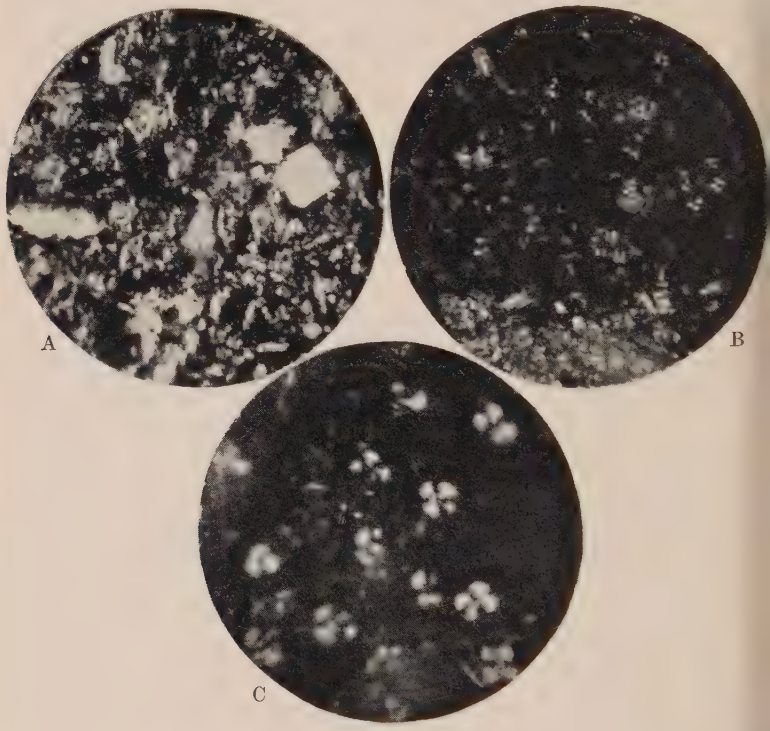


Fig. 1.

A. London clay. Showing detrital quartz grains set in a matrix of fine quart particles and micaceous strands. Crossed nicols. ×200.

B. Speeton clay, Speeton, Yorks. Spherulitic matrix. The anisotropic patch a the bottom is made up of numerous spherulites. Crossed nicols. ×300.

C. Spherulites in Speeton clay. Each spherulite shows the characteristic 'maugl wheel' cross. Crossed nicols. ×1000.

it is 'ironed out'. This will prevent the film from excessive curling whe heated to a higher temperature in the Canada balsam. Meanwhile th 3×1 micro-slide and cover slip are cleaned and placed on the mountin plate.

The flame of the bunsen burner is turned up and at 60° the balsa is applied to the micro-slide and cover slip. When the balsam has sprea out and all air bubbles have been pricked with a needle, the lead weigl

quickly removed, the film is *inverted* and immersed in the balsam on e 3×1 micro-slide. The film is then firmly but carefully pressed down ith *clean* forceps to prevent it from floating up. At 75° the cover ass is lowered over the film and pressed down with a chisel edged atch stick. The mount is kept on the hot plate until the ther-ometer registers 90°; it is then placed on an opal glass tile to cool; e excess of balsam is then cleaned off in the ordinary way with ethylated spirit, and the mount is labelled ready for examination nder the microscope.

The clay sections prepared and mounted as described above have vious advantages, for the sections are easily prepared and the field r investigation is considerably widened.

These clay films, however, are not sections in the ordinary sense of e term, for examination under low powers in polarized light shows at the detrital quartz grains have been pulled out entire, as is evidenced the fact that the central parts of the grains show higher polarization lours than at the edges.

But the chief point of interest in these films is that the matrix can thoroughly explored under high-power objectives, and perhaps further formation may be obtained by using this method than has been ssible hitherto. The author has observed that some clays when mined between crossed nicols under high powers are seen to have a trix composed almost entirely of spherulitic bodies, each of which ows a peculiar 'mangle-wheel' cross. In other clays these authigenic nstituents are entirely absent. As far as can be ascertained these ructures have not yet been recorded. Representatives of both types clay are illustrated in Fig. 1 A–C, and indicate that future research is ely to yield further interesting results which may lead to conclusions geological significance.

Successful preparations have been made from a number of clays, ong which are the following: London clay, Eocene pipe clay, Barton y, Speeton clay, Wadhurst clay, and Oxford clay. It is interesting note that the method has been tried on coal samples with varying grees of success, but it may be possible to make improvements at a er date. An excellent section has been prepared from chalk in which writer has noted that the structures on the exterior of the foramini-al tests can be easily studied.

A note on crystallographic calculations.

By Max H. Hey, M.A., D.Sc.

Assistant Keeper in the Department of Mineralogy of the British Museum.

[Read January 25, 1940.]

In the course of work on the Barker index of determinative crystallography, a number of interesting problems have arisen owing to the selection by a few workers of unusual sets of fundamental angles for their computations. Most of these problems have been of no general application, but one appears to have a wider interest and may prove of practical value in dealing with crystals having curved or striated faces that only admit of accurate measurements along one zone.

This problem was to compute the angles and elements of a monoclinic crystal, using as fundamentals the angles from b (010) to any three faces e, f, g (of known indices) not in the zone [010], and no pair of which are co-zonal with b (fig. 1). These fundamentals do not allow of a solution by spherical triangles, nor by use of the relation $\sin cr \,.\, \tan am \,.\, \tan bq / \sin ra = 1$ with *ad hoc* axes, as is often possible.

The first step in the solution is to locate by the aid of a sketch gnomonogram (fig. 2) a zone through any one of the faces (e) which cuts the zones through b and the other two faces, $[bf]$ and $[bg]$, in faces f', g' such that the gnomonic intercepts ef', $f'g'$ are equal, a step which is always possible, and to calculate the angles bf', bg' by the multiple-tangent relation; let this zone, $ef'g'$, cut the zone [010] in a face D (fig. 1) and let the zones $[be]$, $[bf'f]$, $[bg'g]$ cut [010] in E, F, and G. Then, since $EG = DG - DE$,

$$\cos EG = \cos DE \,.\, \cos DG + \sin DE \,.\, \sin DG \\ - (\cot DE \,.\, \cot DG + 1) \,.\, \sin DE \,.\, \sin DG \quad . \quad \text{(i)}$$

from the triangles Dbe, Dbf', Dbg',

$$\sin D\hat{b}g' = \sin DG = \tan b\hat{D}g' \,.\, \cot bg' \quad . \quad . \quad . \quad \text{(ii)}$$

and

$$\cot^2 DG = \operatorname{cosec}^2 DG - 1 = \tan^2 bg' \,.\, \cot^2 b\hat{D}g' - 1 \quad . \quad . \quad \text{(iii)}$$

[1] r (101), m (110), q (011), R (10$\bar{1}$).

ilarly for DE, DF; and as $DEFG$ are a harmonic quartette by struction,

$$2 \cot DF = \cot DE + \cot DG \quad . \quad . \quad . \quad \text{(iv)}.$$

aring and rearranging,

$$2 \cot DE \,.\, \cot DG = 4 \cot^2 DF - \cot^2 DE - \cot^2 DG$$
$$= (4 \tan^2 bf' - \tan^2 be - \tan^2 bg') \cot^2 b\hat{D}e - 2,$$

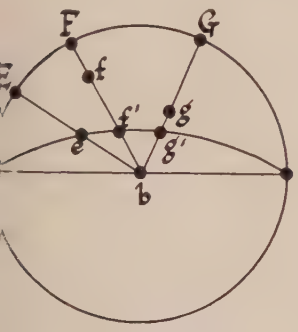


Fig. 1.

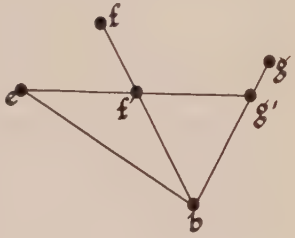


Fig. 2.

substituting this in (i) and eliminating sin DE and sin DG by means i), $b\hat{D}e$ cancels out, giving

$$\cos e\hat{b}g = \cos EG = (4 \tan^2 bf' - \tan^2 be - \tan^2 bg')/2 \tan be \,.\, \tan bg',$$

n is readily solved. As $e\hat{b}g$ completes a spherical triangle, solution now proceed on normal lines, but it is usually more convenient[1] to gn temporary indices g' (011), e (110), F (101), D (10$\bar{1}$) and obtain GD' from the relation

$$\cot cr - \cot ca = \cot cR + \cot ca = \tan am \,.\, \tan bq \,.\, \operatorname{cosec} ca.$$

hile the above relation in its most general form only holds for a set ree polar angles measured from a face-pole which is also a zone-axis (010) of a monoclinic crystal), a restricted form is more generally lable. For if four poles $Defg$ (fig. 3) form a harmonic quartette and the pole of any other zone through D, the above equations hold and ect $e\hat{O}g$ with the angles eO, fO, gO. But as O will not in general be pole of a face, the relations cannot be extended to any three faces; must form a co-zonal harmonic quartette with a face (D) in the of which O is the pole.

t may perhaps be noted here that if be, bg', eg' (fig. 2) are given as funda- als, the most direct solution is given by the relation

$$\cot De + \cot eg' = \cos bg' / \cos be \,.\, \sin eg'.$$

This extension clearly covers the ρ-angles of three faces (on a crysta measured in zone-adjustment) which form a harmonic quartette with face in the zone of reference, enabling the ϕ-angles of the three faces t be calculated, and is equally applicable in the anorthic system.

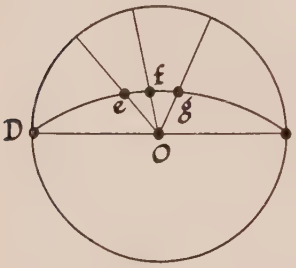


Fig. 3.

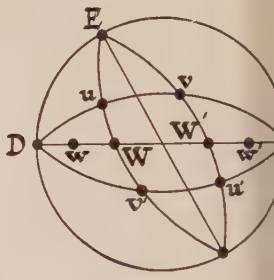


Fig. 4.

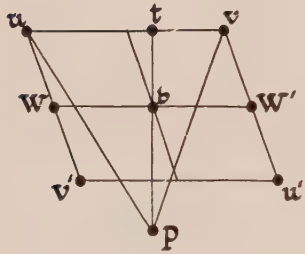


Fig. 5.

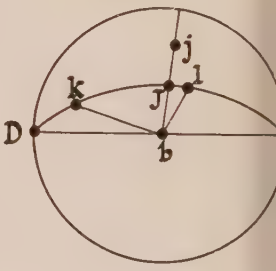


Fig. 6.

Another problem of some interest, though of less general value, the calculation of the elements of a monoclinic crystal from the angl from a face D in the zone [010] to any two faces, u, v (of known indice in one zone through D and a third face w in the zone $[Db]$ (fig. 4).[1] He again it is not possible to solve by spherical triangles in the normal way

[1] The measurement of ammonium cobalticyanide by V. von Lang (Sitzungsbe Akad. Wiss. Wien, 1862, vol. 45, Abt. II, p. 107) includes so few angles that t only available fundamentals are of this type. The same selection of fundamenta was made for hydrobromcinchene by W. Muthmann (Zeits. Kryst. Min., 188 vol. 15, p. 391).

[2] Where the given angles are DW, uW, vW (fig. 4), solution is possible by drawi zone-circles through u and v to cut $[DWb]$ at right angles; the final solution $\sec D\hat{W}u = 2\cot DW/(\cot uW - \cot vW)$. Unless the angle $D\hat{W}u$ differs consid ably from 90°, this selection of fundamentals is very unfavourable, but was us for potassium cobalticyanide by H. Topsøe, Sitzungsber. Akad. Wiss. Wie 1872, vol. 66, Abt. II, p. 43.

et the zone $[uv']$ meet $[Dwb]$ in W and the zone $[010]$ in E; the indices W and the angle DW may readily be calculated. Now let the gnomic angle point of the zone $[Duv]$ be P and the projection radius of gnomonic projection (fig. 5) R, and let Pb meet the zone line $[Duv]$. Then $Pt = R.\sec b\hat{D}u = R.\sec b\hat{D}v$, and $P\hat{u}t = Du$, $P\hat{v}t = Dv$. m the plane triangle Put, $ut = Pt.\cot P\hat{u}t = R.\sec b\hat{D}u.\cot Du$, similarly $vt = R.\sec b\hat{D}u.\cot Dv$. But

$$ut+vt = uv = 2bW = 2\,R.\,\cot DW.$$

nce $$\sec b\hat{D}u = 2\cot DW/(\cot Du + \cot Dv).$$

$b\hat{D}u$ completes a spherical triangle, solution can now proceed on mal lines.

astly, one special case in which a simple solution is possible may be tioned.[1] In a monoclinic crystal, angles from b (010) to any two s j, k, and the angle kl from one of these faces to a third face not in er of the zones $[bj]$, $[bk]$ are given (fig. 6). If j is not in the zone $[kl]$ the zones $[bj]$, $[kl]$ cut in J, the indices of which, and the angle bJ, then calculated; and let the zone $[kl]$ cut $[010]$ in D. Then the armonic ratio $\sin Dk.\sin lJ/\sin DJ.\sin lk$ may be calculated; let it $= p/q$. Now $\cos bk/\cos b\hat{D}k = \sin Dk$, and $\cos bJ/\cos b\hat{D}k = \sin DJ$; stituting in the anharmonic ratio, $\cos bk.\sin lJ/\cos bJ.\sin lk = p/q$, nce lJ may be calculated, and then solution proceeds normally ugh Dk and the triangle bDk.

[1] Exemplified by 3:3-dimethyl-2-(α-oximinoethyl)-pseudoindol (G. Boeris, cited P. Groth, Chem. Kryst., 1919, vol. 5, p. 552).

The composite dike at Brockhill, Worcestershire.[1]

(With Plate XXIII.)

By J. H. Taylor, M.A., Ph.D., F.G.S.

Geological Survey of Great Britain.

[Read March 7, 1940; communicated by Dr. J. Phemister.]

(1) *Introduction.*

At Brockhill in Worcestershire, some 11 miles west of Droitwich in the valley of the river Teme, a small dike of igneous rock i intruded into the red marls and sandstones of the Downtonian Series.

The dike was figured and described by Phillips[2] in 1848. On the Ol Series one-inch Sheet 55 N.E. it was indicated as having a very limite outcrop on the eastern side of the river Teme; but a report of an excur sion to Brockhill in 1874[3] records the presence of igneous rock on th opposite bank. The intrusion was examined during the resurvey on th six-inch scale of the New Series one-inch map, Sheet 182 (Droitwich) and is of interest both on account of its petrographic character and it remoteness from other igneous rocks. It has recently been traced b magnetic methods for a distance of over three-quarters of a mile.[4]

(2) *Field Relations.*

The principal exposures are indicated on the sketch-map (fig. 1) whic shows the trend of the dike to be some 8–10° north of west and sout of east. The largest and most important outcrop is a quarry som 250 yards north-west of Brockhill farm, on the east bank of the rive Here a 70-foot vertical section shows the dike cutting Downtonian mar and sandstones and inclined at about 70–75° to the south. Near th base of the pit much of the dike has been quarried away and the centr

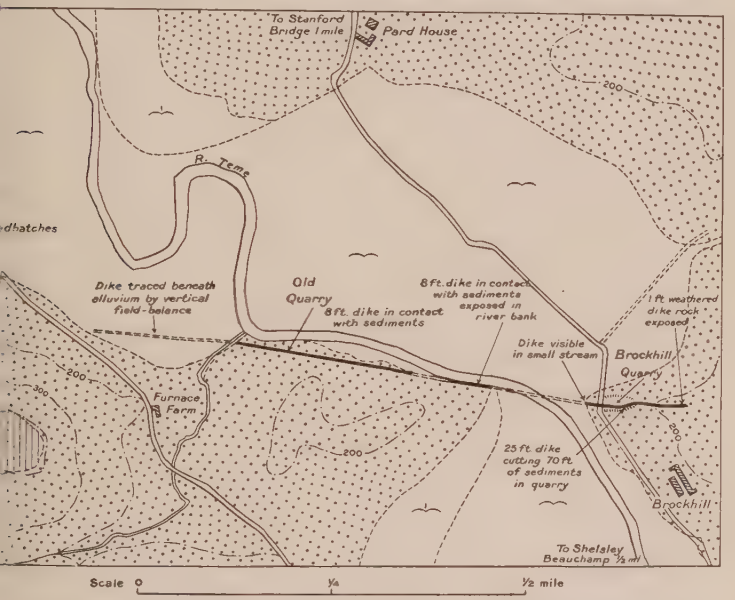
[1] Published by permission of the Director, Geological Survey of Great Britain.

[2] J. Phillips, The Malvern Hills, compared with the Palæozoic districts of Abbe ley, Woolhope, May Hill, Tortworth, and Usk. Mem. Geol. Surv. Great Britai 1848, vol. 2, part 1, pp. 155–158.

[3] Trans. Worcestershire Nat. Club, 1874, vol. 1, pp. 211–212.

[4] A. F. Hallimond, Magnetic observations on the Brockhill dyke. Bull. Geo Surv. Great Britain, 1939, no. 2, pp. 85–92.

mpletely obscured by rubble. Higher up the face it is well exposed reaches a maximum of about 25 feet in thickness. In the main it moderately coarse, dark-grey to black dolerite which weathers to sh-brown rock speckled with white felspar and analcime and gives to a brownish soil lighter in colour than that derived from the



. 1. Sketch-map of the Brockhill dike. Alluvium and low-terrace gravels). Dittonian (ruled); Downtonian (stippled). Course of dike indicated in

ning sediments. The dike is well jointed parallel to the contacts, ell at right angles to them, and this rectangular arrangement of inting may have assisted in the inception of the spheroidal weather- hich is common. The rock appears very homogeneous and is finer ed only for an inch or two along each contact: this fine-grained n (p. 543) is quite distinct in character from the main mass of ke.

e country-rock, which here has a slight dip to the north of west, ts of red marl and marly micaceous felspathic sandstone and les, near the top of the quarry, a thin cornstone band containing agments. All these rocks have suffered some degree of altera- o a distance of about 30 feet on both sides of the dike. Near the

contact, both marls and marly sandstones have been converted into co
pact dark rocks, often closely jointed at right angles to the junction w
the dike. A common and striking form of alteration of the marls, seen
its best in the upper part of the section on the south (hanging) wall
the dike, has given rise to fine-grained, dark-purplish rocks which sh

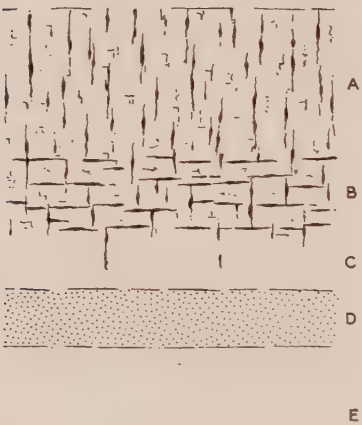


Fig. 2. Section of metamorphosed sediments from half-way up face of Brockhill quarry.

A. Soft marl, much vertical piping by pale greenish material.

B. Soft marl, vertical and horizontal joints infilled with pale greenish material.

C. Hard marl, few pipes.

D. Sandstone.

E. Hard siltstone; no piping.

numerous cream-coloured to p
green more coarsely crystall
streaks and blotches. Many
these streaks are elongated ve
cally and, being roughly circu
in cross-section, bear a superfi
resemblance to pipe amygda
Their distribution is apparen
governed by differences in
composition of the marls as s
gested by the section illustra
in fig. 2. Near the top of the
the cornstone band, which is
than one foot thick, has been c
verted into a compact yellow
crystalline lime-silicate rock. I
difficult to match up the s
ments on the two sides of the d
and it is possible that the intrus
has taken place along a sm
fault.

At several points eastward
the quarry, fragments of weathe
dolerite and altered sediment
visible. About 70 yards to the
weathered dike rock is exposed, and unaltered red marl turned ou
burrows 2–3 yards farther down the slope shows that the metamor
effects produced by the dike are here comparatively slight. The
exposure in this direction is some 120 yards east of the quarry wh
one foot of fine-grained weathered dike rock is exposed.

West of the Brockhill quarry the dike disappears under the alluv
of the river Teme, but in dry seasons is visible as a reef running obliq
across the river. On the opposite bank, some 300 yards west of the qua
it is again exposed in contact with red and green marls both to the n
and south. Here the thickness of the dike has diminished to 8 f

roidal weathering is prominent, and jointing across the dike is much r developed than that parallel with its length. The intrusion has a ıct chilled margin 6 inches or so wide, but the zone of contact- morphism in the marl is very narrow, never reaching as much as oot in width. The alteration is slight and is of the same order as 25–30 feet from the contact in the main quarry, that is, the marl een indurated to form a compact red-brown to purple-brown rock. e most westerly exposure seen is in a small coppice 750 yards west rth of the main quarry. Here 8 feet of dike rock with a 6-inch d margin is seen in contact with grey shaly indurated sediment south side. A short distance to the west the dike again disappears th the alluvium and its further course has been traced by magnetic ods for several hundred yards.

(3) *Petrography.*

The igneous rocks.—The rock from the central portion of the dike main quarry is a teschenite with abundant pyroxene and felspar, dinate olivine, and interstitial analcime and zeolites (pl. XXIII,). The pyroxene is a slightly purplish titanaugite which forms with a strong tendency to idiomorphism and also occurs fre- ly in groups of subhedral crystals. Olivine is almost completely d to deep green or olive-green serpentine: in many cases the out- are irregular, but occasionally the characteristic shape of olivine erved (17672).[1] The amount of felspar varies and while usually proportion of 30–40 per cent. may fall so low that the rock might assed as a picrite (17949). It is predominantly plagioclase but es a considerable proportion of orthoclase. The plagioclase forms ely arranged prisms up to about one millimetre long, centrally of dorite composition, but zoned marginally to oligoclase. The prisms ften replaced in the centre by fibrous green chlorite and are pene- l by strings of analcime. Orthoclase builds stout clear prisms and mantle the plagioclase (17951). Analcime is common in the inter- between the felspars and also occupies large residual spaces. Very , a short rectangular prismatic outline within an area of analcime sts the possibility of original nepheline though no more definite nce of the presence of this mineral could be found. Both felspar nalcime are commonly replaced by pale brown, fibrous radiat- atrolite: in specimen 17949 granular chabazite is also present

[1] ese numbers refer in all cases to the English series of microscope slides at the ical Survey Office, Exhibition Road, South Kensington, London.

interstitially. Iron-ore, probably a titaniferous magnetite, is abunda and is sometimes bordered by irregular flakes of brown biotite. Accesso minerals include many long needles of apatite and an occasional pri of zircon.

An analysis of the teschenite has been made and is given bel (col. I), together with analyses of a teschenite from Blackburn, L lithgowshire (A), and of the analcime-dolerite of Clee Hill, Shropshire (for comparison.

	I.	A.	B.
SiO_2 ...	46·28	45·71	48·4
TiO_2 ...	2·56	1·64	3·1
Al_2O_3 ...	14·90	15·23	13·4
Fe_2O_3 ...	3·52	2·84	4·0
FeO ...	7·13	6·93	8·5
MnO ...	0·54	0·54	—
MgO ...	6·12	8·11	6·5
CaO ...	6·58	7·34	8·6
Na_2O ...	4·49	3·96	3·1
K_2O ...	1·72	1·31	2·1
$H_2O > 105°$ ...	4·36	4·70	2·2
$H_2O < 105°$ ...	1·28	1·54	
P_2O_5 ...	0·74	0·47	—
CO_2 ...	0·00	0·00	—

	I.	A.
SO_3 ...	0·01	—
Cl ...	trace	trace ?
F ...	0·04	—
S ...	—	0·08
FeS_2 ...	0·20	—
Cr_2O_3	0·00	0·02
V_2O_3 ...	—	0·03
(Ni,Co)O	—	0·02
BaO ...	0·05	0·04
SrO ...	—	trace ?
Li_2O ...	—	trace
	100·52	100·51
Less O for F	0·02	
	100·50	

I. Teschenite. Dike at quarry 250 yards north-west of Brockhill farm, Worcest shire. Analyst, C. O. Harvey.

A. Teschenite. Probably Carboniferous sill. Leckstone quarry, Blackbu Linlithgowshire. Analyst, W. Pollard. Summ. Progr. Geol. Surv. Uni Kingdom, for 1905, 1906, p. 74; Geology of the Neighbourhood of Edinbur Mem. Geol. Surv. Scotland, Sheet 32, 1910, p. 299.

B. Analcime-dolerite. Clee Hill, Shropshire. Analyst, J. H. Player, in F. Hatch, Text-book of petrology, 2nd edit., London, 1892, p. 179.

The norm, mode, and Niggli values for the Brockhill teschenite a as follows:

Norm.		Mode.		Niggli values.	
or	10·01	orthoclase	5·0	si	117
ab	30·92	plagioclase	29·4	al	22·2
ne	3·98	serpentinized olivine	4·2	fm	46·0
an	15·29	augite	19·8	c	17·9
di	10·32	analcime	16·0	alk	13·8
ol	12·48	natrolite	2·6	qz	−38
il	4·86	chlorite	11·5	k	0·20
mt	5·10	biotite	1·0	mg	0·50
ap	1·68	iron-ore	9·1	c/fm	0·39
	94·64	apatite	1·4		
			100·0		

Sp. gr. 2·71 Camptonose Symbol III. 5. 3. 4.

ne Brockhill rock is similar in chemical composition to the teschenite lackburn, a sill of Permo-Carboniferous age in the Midland Valley cotland: compared with the Clee Hill rock it is poorer in silica and and richer in alkalis.

ne marginal rock proves to be a fine-grained quartz-dolerite or lt (pl. XXIII, fig. 2). It is composed of stout mutually interfering ns of plagioclase and numerous idiomorphic or hypidiomorphic ns of colourless augite, which may be fresh but are usually traversed racks, along which serpentine is developing, and speckled with many ules of iron-ore. In some specimens the pyroxene is altered to ly birefringent fibrous bowlingite. The plagioclase is labradorite, d towards the margin to oligoclase, and, while of uniform grain in idual specimens, the prisms range from about 0·3 mm. to 1 mm. in h. Augite shows continuous gradation in size from microlitic ns to large crystals, 2 mm. long, in the same rock-section.

ere is considerable divergence in the proportion of the minor con- nts which include alkali-felspar, quartz, chlorite, iron-ore, and ntinous pseudomorphs after olivine. In specimen 17948, which s many small prisms of green fibrous material after olivine or per- orthopyroxene, quartz is present in very small quantity as inter- l grains, alkali-felspar is observed as partial mantles to oligoclase s small prisms in quartz, and spherulitic chlorite is present but bundant. Specimens 17944, 17572, and 17953 show decrease in roportion of ferromagnesian minerals, and an increase in alkali- r, including perhaps cryptoperthite; quartz is present inter- lly. Further variation is shown by specimens 17951 and 17952, in alkali-felspar and interstitial spherulitic chlorite are abundant, the ferromagnesian minerals are almost entirely replaced by tic material.

n-ore, which is abundant in all sections, probably includes both ite and magnetite, and is leucoxenized in the more alkalic speci- Accessory constituents include clear red-brown biotite and ce.

oss the Teme, where the dike is much narrower, the rock is ctly finer grained. A specimen from the centre of the dike (17675) altered ferromagnesian minerals set in a groundmass of small ine-labradorite laths. A considerable amount of augite is still nizable, but olivine has been completely replaced by yellow-green ntine and chlorite. Iron-ore is plentiful and some epidote occurs alteration product of ferromagnesian minerals and felspar. There

is no trace of either analcime or quartz. At its margin the dike is st more decomposed. Large phenocrysts or rounded masses which no consist of calcite with subordinate chlorite are set in a fine-grain groundmass of felspar microlites, chlorite, and iron-ore. In some cas (17676) the crystal outlines of both augite and olivine are recognizab in the calcite-chlorite pseudomorphs.

(*b*) *The metamorphic rocks.* –The commonest type of hornfels is a altered felspathic sandstone consisting of grains of quartz and su ordinate felspar surrounded by finely divided aggregates of quart felspar, and abundant ferromagnesian minerals which are not alwa determinable. The quartz is present as subangular grains some of whi are seen to have grown, incorporating at the edges minute specks of t other minerals. Many of the quartz grains are surrounded by fring having the form of tridymite laths (pl. XXIII, fig. 5). The tridymite h now inverted to quartz which is optically continuous with the pare grain. The larger quartz grains are separated by a fine-grained mosa of quartz and alkali-felspar. Of the coloured constituents, much yellowish-green chlorite, increasing in amount towards the conta Small scales of red-brown biotite, about 0·02 mm. across, are prese and ragged prisms of green hornblende are also recognizable, wh minute octahedra of iron-ore are very abundant. In 17953 what appe to be yellowish pinitic clots after cordierite are present.

A similar development of tridymite fringes to quartz grains is record from siliceous xenoliths in the igneous rocks of Vulcano,[1] Braefoot Fife,[2] and Mull.[3] Bowen[4] and Larsen[5] have expressed the opinion th the presence of this mineral is not necessarily an indication of hi magmatic temperature, and this is borne out in the present instan where it is associated with what is essentially a low-temperature mine assemblage, though there is a probability of late chloritization.

Where the country-rock was marl rather than marly sandstone, t percentage of coloured minerals in the hornfels is higher, much of t brown and colourless mica of the original sediment appears unaltere and there is a great deal of indeterminable brown material. The crea

[1] A. Lacroix, Les enclaves des roches volcaniques. Macon, 1893, pp. 168–169

[2] R. Campbell, T. C. Day, and A. G. Stenhouse, The Braefoot outer sill, F Trans. Edinburgh Geol. Soc., 1932, vol. 12, pp. 360–361; 1934, vol. 13, pp. 166–1

[3] H. H. Thomas in Tertiary and post-Tertiary geology of Mull, Loch Aline a Oban. Mem. Geol. Surv. Scotland, 1924, pp. 198, 274.

[4] N. L. Bowen, Geologic thermometry. Chapter X in The laboratory investi tion of ores (edited by E. E. Fairbanks). New York, 1928, pp. 180–184.

[5] E. S. Larsen, The temperature of magmas. Amer. Min., 1929, vol. 14, pp. 86-

ured pipes and blotches which so commonly occur in the altered
s are of special interest (pl. XXIII, fig. 6). The central portion consists
rge plates of calcite and analcime, the latter showing complicated
ning effects: commonly the two minerals are intergrown in a manner
esting replacement (17680, 17781). Scattered through both is much
-opaque material consisting of greenish-brown chlorite with mean
ctive index 1·556, and numerous small colourless garnets, hardly
larger than 0·02 mm. across. This clear central portion is surrounded
white opaque zone composed largely of finely divided carbonate
small garnets, and this in turn passes outwards into a zone of reddish
ed mudstone which passes into the normal metamorphic rock
ibed above.

e only other type of hornfels present is that resulting from the
ation of the cornstone band mentioned on p. 540. This has been
erted into what is essentially a quartz-calcite-garnet-rock (17681–3).
l crystals of a colourless grossular garnet are scattered through the
in such numbers as to render parts of it almost opaque and are
lded both in large irregular plates of calcite and in a fine-grained
z mosaic. Frequently a thin ring of somewhat more coarsely
alline quartz separates the calcite plates from the quartz mosaic.
green chlorite is not uncommon and often has small granules of
etite associated with it, while occasional wisps of brown mica and
s of epidote are also present.

(4) *Age of the Intrusion.*

e only field evidence as to the age of the Brockhill dike is that it
st-Downtonian. Other analcime-bearing rocks of the Midland
ies include the dolerites and basalts of Clee Hill, Wednesfield,
Hill, Rowley Regis, and Little Wenlock, now commonly regarded
Carboniferous age,[1] and it seems probable that the Brockhill
sion may be assigned to the same period. Similar rock types are
found among the Carboniferous intrusions of the Midland Valley
otland, though in that region there appears to have been a con-
able time interval between the intrusion of the teschenites and the
z-dolerites.

many ways the Brockhill intrusion bears a close resemblance to

. W. Pocock, The age of the Midland basalts. Quart. Jour. Geol. Soc. London, vol. 87, pp. 1–12. See also Shrewsbury district. Mem. Geol. Surv. Great n, 1938, appendix VI, p. 281.

the basic dike at Bartestree near Hereford.[1] This is also composi consisting of teschenite, olivine-free dolerite, and basalt, intimat associated with one another and regarded by Reynolds as success intrusions. Small quantities of quartz in the dolerite near the cont are presumed to have been picked up from the Old Red Sandstone i which the dike is injected. Slides 7604, 7606 of metamorphosed ma sandstone close to the contact with the Bartestree dike show tridym fringes to the quartz grains similar to those in the contact zone of t Brockhill dike.

(5) *Relations of the teschenite, quartz-dolerite, and country-rock.*

The quartz-dolerite shows variable contact relations to the count rock. In some cases (17572, 17673) the contact is sharp. The igne rock shows only a slight diminution of grain-size, the country-ro maintains its hornfelsed sedimentary character. Between the t distinct rocks is a zone 0·5–1 mm. wide, which is sharply defined difference in grain-size and by marginal concentration of small pris of augite or its pseudomorphs from the quartz-dolerite, and which sho abrupt difference in texture and composition from the country-ro (pl. xxiii, fig. 3). The origin of this zone is uncertain, but it is suggest that it represents sediment to which magmatic material has been adde It is clear that the quartz-dolerite has been intruded as molten magm along this contact while the country-rock was hot.

In other cases (17945–7, 17952) there is a passage between conta altered sediment of a muddy siltstone type and felspathic fine-grain rock of quartz-doleritic affinity resembling craignurite, and one secti is made up partly of altered sediment, partly of fine-grained holocryst line igneous rock and partly of rock which shows igneous texture y includes contact-altered quartz with tridymite fringes (17947). 17952 the transitional zone shows a lathy plagioclase base containi many prismatic pseudomorphs in yellow chlorite and greatly obscur by dissemination of similar material (pl. xxiii, fig. 4). Abundance small fresh granules and prisms of pyroxene suggest contamination incorporation of a pyroxene-hornfels (17945–6). In several cases coarser grained quartz-dolerite or basic craignurite shows a sha contact against fine-grained contaminated igneous rock of similar ty (17944, 17952), and it seems as if the quartz-dolerite had been intrud against a metasomatized semi-igneous skin of the country-rock.

[1] S. H. Reynolds, The basic intrusion of Bartestree. Quart. Jour. Geol. S London, 1908, vol. 64, pp. 501–511.

lar state of affairs is shown in 17953, where the transition zone
ists of laths of plagioclase and alkali-felspar, abundant chlorite
iently as long prisms disposed roughly at right angles to the contact,
much finely divided iron-ore.

ven specimens of the contact were collected from different posi-
and all showed the intrusive rock to be of the quartz-dolerite type.
henite has not been seen in contact with the sediments nor was any
of a chilled junction between teschenite and quartz-dolerite
rved. Specimens 17953–5, representing a three-inch depth of the
us rock at the northern contact near the base of the quarry, form
ies showing a gradual passage between the teschenite and quartz-
ite. Specimen 17953, in contact with the sediment, is a quartz-
ite with abundant plagioclase laths, fresh augite, iron-ore, inter-
l alkali-felspar, some green serpentinous material, and a little
tz: on the side of this section, away from the contact, chlorite
mes abundant in interstitial spherulitic aggregates. Specimen 17954
quartz-free dolerite containing a higher proportion of interstitial
rulitic chlorite than 17953, and carrying, towards the interior of the
prismatic and rounded pseudomorphs in semi-opaque orange ser-
inous material; biotite also increases markedly in this direction.
section 17955, about one inch farther into the dike, shows on the
close to 17954 a rock similar to the latter, but within a few milli-
s a little analcime appears, and this mineral, together with pseudo-
hs after olivine, rapidly becomes so abundant that on the other
of the section the rock is a normal teschenite.

om a consideration of the thin sections two points are evident:

that the quartz-dolerite was intruded as a molten magma which reacted locally with the sediment to form a thin metasomatized zone;

that the teschenite and the quartz-dolerite were intruded almost simultaneously, since there is a gradual passage from one to the other.

e passage relations of the quartz-dolerite to the teschenite, and the restricted development of the former—confined to a two-inch zone ther side of the dike—do not encourage the hypothesis that the rock types represent successive intrusions. A possible explanation at the quartz-dolerite represents a modification of the teschenitic na by reaction with the country-rock. An example of quartz-ite formed in this manner is recorded from the Braefoot outer sill e (Campbell, Day, and Stenhouse, loc. cit.), where acidification of

teschenitic magma by abundant xenoliths of sandstone and quartzi has given rise to a rock approximating in composition to quart dolerite. That the modification of the teschenitic magma cann have taken place in situ at Brockhill is obvious from the sharp natu of the contact between country-rock and quartz-dolerite. It is possibl however, that reaction between teschenite and country-rock was oper tive during the passage of the magma through the sediments.

The richness of the teschenitic magma in volatile constituents is show both by abundance of zeolites in the igneous rock and by analcimiz tion of the contiguous marls, and this may have provided a mediu for exchange of materials between magma and sediment, silica bei added to the magma. It is suggested that this acidified magma mounte in advance of the main uncontaminated teschenitic magma and coate the walls of the fissure, in places chilling against the country-rock, others reacting further with it. Local contact of quartz-doleritic ro with chilled facies of the same type suggests a pulse-type of advan through the fissure. The main influx of magma which followed imm diately would be protected from the country-rock and would come in place as teschenite forming the central portion of the dike.

In conclusion, the author wishes to record his indebtedness to Dr. Phemister for taking the photomicrographs and for much kind assistan and criticism.

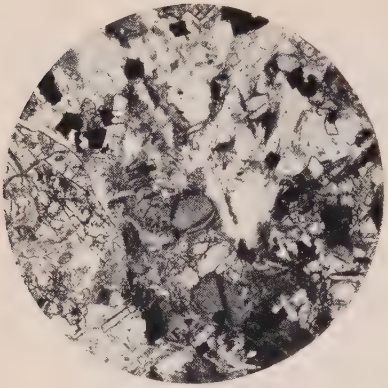


Fig. 1.

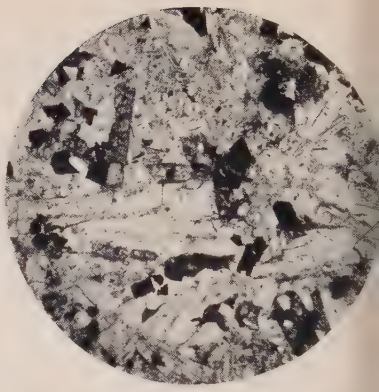


Fig. 2.

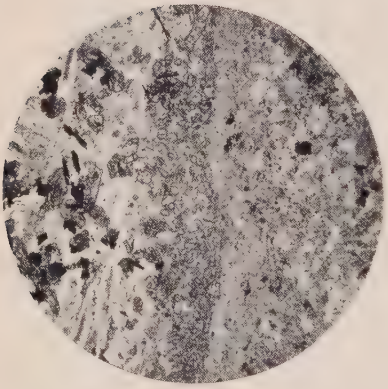


Fig. 3.

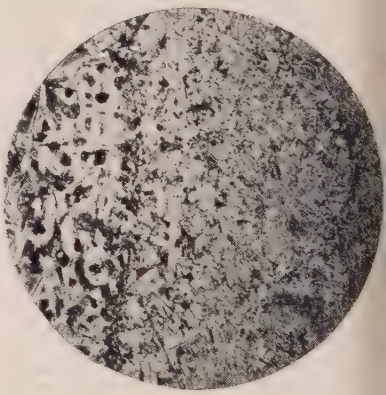


Fig. 4.

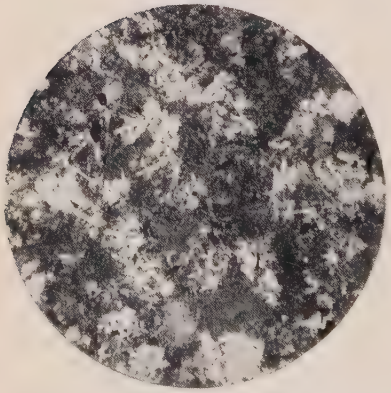


Fig. 5.

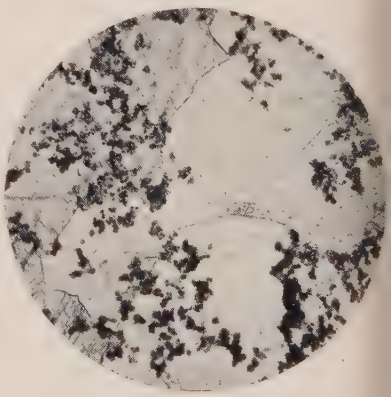


Fig. 6.

J. H. Taylor: Brockhill Rocks.

Explanation of Plate XXIII.

Photomicrographs of Brockhill rocks.

(E numbers refer to microscope slides and M numbers to photographs in the Geological Survey collection.)

Fig. 1. Teschenite (E 17672, M 2120). Shows serpentinized olivine, titanaugite, iron-ore, prismatic felspar, and interstitial analcime. Ordinary light. ×20.

Fig. 2. Quartz-dolerite (E 17673 duplicate slide, M 2121). Shows prisms of zoned plagioclase, prismatic augite, chlorite, iron-ore, and patches of fine-grained quartzo-felspathic mesostasis. Ordinary light. ×20.

Fig. 3. Junction of quartz-dolerite and marly sandstone (E 17572, M 2124). Quartz-dolerite (on left) contains lathy plagioclase, augite, chlorite, iron-ore, and little quartz. The sediment contains quartz grains separated by quartz-felspar mosaic and chloritic material. Along the junction is a 0·5 mm. zone in which augite is concentrated. Ordinary light. ×20.

Fig. 4. Passage rock between quartz-dolerite and muddy siltstone (E 17952, M 2123). Quartz dolerite (on left) consists of lathy plagioclase, some augite, much chlorite, and iron-ore. This type ends by concentration of small prisms of chloritized augite against a more granular rock of same type which in turn passes into a fine-grained turbid lathy plagioclase-rock with much chlorite both interstitially and as prismatic pseudomorphs. A short distance outside the field of the photograph this rock type passes into hornfelsed muddy sediment. Ordinary light. ×9.

Fig. 5. Hornfelsed sandstone (E 17947, M 2125). Shows quartz grains, many with acicular offshoots of tridymite, fine-grained quartz-felspar mosaic, and much chloritic material. Crossed nicols. ×30.

Fig. 6. Light coloured patch from contact altered marls (E 17680, M 2122). Showing large plates of cleaved calcite and in the lower part of the photograph clear analcime. Through these is scattered greenish-brown chlorite surrounding numerous small garnets. Ordinary light. ×28.

Iron-rich kornerupine from Port Shepstone, Natal.[1]

By J. E. de Villiers

Geological Survey of the Union of South Africa.

[Read March 7, 1940; communicated by the editor.]

Occurrence.—A very interesting kornerupine-bearing rock was sent b Mr. W. H. Cross during 1938 to the Geological Survey for identificatio The material, of which about 800 grams were available for study, wa stated to have been found in the Port Shepstone district. The occurren has, however, not been visited by the writer.

The hand-specimens examined were all somewhat weathered. Macr scopically these consisted of an intergrowth of grey, columnar crysta of kornerupine, up to 5 centimetres in length, and adhering iron-staine quartz. Shiny 'books' of biotite occur both in the kornerupine and th quartz, while small patches and specks of dark brown tourmaline an bluish grandidierite were observed enclosed in the kornerupine. Th nature and texture of the component minerals make it seem likely tha the rock is of pegmatitic origin and that contact assimilation of iro and magnesium has played a part in its formation.

Physical properties.—Cleavage, prismatic, distinct. H. $6\frac{1}{2}$, sp.gr. 3·44 Fuses at 6 to a black, moderately magnetic globule. Colour, greyish i hand-specimen, light yellow in powder. Moderately magnetic. Th mineral is fairly friable owing to advanced and incipient alteratio along cracks, and contains fairly abundant inclusions.

The specific gravity was obtained by matching the crushed miner with a heavy liquid until neither sinking nor floating occurred, an measuring the specific gravity of the liquid immediately. The resu given is the mean of several determinations, which range from 3·438 t 3·446, and is corrected for water at maximum density.

Crystallographic properties.—The following faces were observed o crystal fragments: *a*(100), *b*(010), and *m*(110). These gave poor refle tions on the goniometer. The measurements obtained were in accordan

[1] Published by permission of the Hon. The Minister of Mines, Union of Sou Africa.

orthorhombic symmetry, the mean of a large number of determina-
s yielding the result (100):(110) = 40° 30′ (accuracy ±15′), corre-
nding to the axial ratio $a:b = 0{\cdot}854:1$.

ptical properties.—Fragments oriented on the goniometer were
oned and the following optical properties noted under the petro-
hic microscope:

$\alpha = c$, $\gamma = b$. $2V\alpha$ 48° (±4°), Mallard's method. $r<v$.
eochroism, α and β colourless or nearly so, γ light amber (yellow
with some brown and green).
efractive indices were measured on conoscopically oriented grains
or cleavage fragments in sodium-light:

α 1·682, β 1·696, γ 1·699 (all ±0·002).

a check on the accuracy of these indices the optic axial angle was
lated. This gave $2V\alpha \pm 50°$. No appreciable variation from the
e properties was noted in the material available for examination.
low is listed in tabular form the principal properties of kornerupine
the various localities known.

BLE I. Physical, optical, and crystallographic properties of kornerupine.

H.	Sp. gr.	α.	β.	γ.	$2V\alpha$.	$a:b:c$.	
6½	3·445	1·682	1·696	1·699	48°	0·854 : 1	—
6½	3·27	1·6650	1·6766	1·6770	19½°*	0·860 : 1*	—
—	3·28	—	—	—	—	0·865 : 1 : 0·423	
7	3·345	1·6711	1·6826	1·6840	28°48′	0·862 : 1 : 0·435	
6½	3·273	—	—	—	19°*	0·854 : 1	—

Port Shepstone, Natal. Analysis I (table II) by C. J. van der Walt, Division of Chemical Services, Pretoria.

Fongay, Madagascar. Analysis II by F. Raoult in A. Lacroix, Minéralogie de Madagascar, 1922, vol. 1, p. 396.

Waldheim, Saxony (var. prismatine). B. Gossner and F. Mussgnug, Neues Jahrb. Min., Abt. A, 1928, Beil.-Bd. 58, p. 227. [M.A. 4–109.]

Waldheim, Saxony (var. prismatine). J. Uhlig, Zeits. Kryst. Min., 1910, vol. 47, p. 215.

Fiskernæs, Greenland. J. Lorenzen, Meddelelser om Grønland, 1884, vol. 7, p. 19.

* These figures were calculated by the writer from relevant data.

emistry.—The kornerupine for chemical analysis was crushed and
ed by separation with heavy liquids. The resultant product was
on microscopic examination to be of fair purity, the total im-
es (consisting of ilmenite with some grandidierite, quartz, &c.)
estimated at less than 1%.

TABLE II. Chemical analyses of kornerupine.

	I.	II.	III.	IV.	V.
SiO_2	29·53	31·09	33·20	30·61	30·90
B_2O_3	3·5	3·59	—	—	—
Al_2O_3	40·97	38·17	42·36	42·11	46·79
Fe_2O_3	11·66	2·02	0·30	2·21	2·02
FeO	1·72	0·73	5·81	4·51	—
MnO	0·08	—	—	—	—
MgO	10·90	22·51	11·76	15·23	19·46
CaO	nil	0·51	—	—	—
Na_2O	0·70	1·36	5·07	1·85	—
K_2O	nil	0·08	0·83	0·85	—
TiO_2	0·44	—	—	0·30	—
P_2O_5	0·12	—	—	—	—
H_2O+...	0·67	0·10	1·60	1·94	1·30
H_2O-...	—	—	—	0·14	—
	100·29	100·16	100·93	99·75	100·47

I–V, localities and references at foot of Table I.

Various attempts have been made in the past to find a formula th adequately expresses the variations in the composition of kornerupin and the following general expressions have been put forward:

(1) J. Lorenzen (1884) ... ... $MgAl_2SiO_6$.
(2) J. Uhlig (1910) ... ... $H_3NaMg_6Al_{12}Si_7O_{40}$.
(3) B. Gossner & F. Mussgnug (1928) ... $4MgSiO_3.3Al_2O_3$.
(4) A. Lacroix (1922) ... ... $(SiO_4)_7Mg_8(Al,B)_{12}O_{12}$.

Only the analyses by van der Walt and Raoult show the presence boron. Since, however, the Fiskernæs and Waldheim materials close resemble minerals analysed by these workers, it must be assumed th boron is a constant constituent of kornerupine. It may further observed: (i) Lorenzen apparently did not analyse for alkalis and ga all his iron as Fe_2O_3; (ii) the comparatively high molecular percenta of silica in the analysis of Gossner and Mussgnug is probably due an admixture of quartz in the analysed material, since the presence this mineral is recorded by these writers.

In an attempt to deduce a suitable expression for the composition kornerupine, reliance must therefore be placed chiefly on the analy by Raoult and van der Walt.

Inspection of table II shows that the kornerupine from Port Shepsto differs from that of other localities chiefly in having a higher ferric ir and lower magnesia content. The Waldheim prismatine also has a l percentage of magnesia, but this deficiency is balanced by a high content of ferrous iron and sodium. As there would thus appear to

n for doubt as to whether the iron in the Port Shepstone mineral is fly ferric and not ferrous the following report by Mr. van der Walt ppended.

have carried out the iron determination three times and obtained lts that show satisfactory agreement. There is, however, a possi- y that the mineral is not completely decomposed by HF and O_4.'

ne question as to whether the water must be regarded as constitu- al or absorbed cannot be answered with certainty. In view, however, ne small amounts usually present (in one case practically negligible) as decided to disregard the water in an attempt to arrive at a general ula.

ne lattice constants for prismatine were determined by Gossner and sgnug. These are a 13·86, b 16·02, c 6·78 Å. Kornerupine from ernæs gave c 6·8 Å. As the axial ratio $a : b$ of kornerupine from ngay and Port Shepstone agrees closely with that of Waldheim and ernæs (see table I) it can be assumed that the unit cells of the various ties of kornerupine are of nearly equal dimensions. These constants the density enable the unit-cell contents of the Itrongay and Shepstone material to be calculated.

TABLE III. Empirical unit-cell contents of kornerupine.

Port Shepstone. Atomic ratio × unit-cell volume × 3·44 / 1·649 × 98·67				Itrongay. Atomic ratio × unit-cell volume × 3·27 / 1·649 × 100·06			
Mol. ratios.	Atomic ratios.	Metal atoms.	Oxygen.	Mol. ratios.	Atomic ratios.	Metal atoms.	Oxygen.
0·4915	0·4915	15·64	31·28	0·5177	0·5177	15·45	30·90
0·0503	0·1006	3·20	4·80	0·0516	0·1032	3·08	4·62
0·4017	0·8034	25·56	38·34	0·3746	0·7492	22·35	33·52
0·0730	0·1460	4·65	6·98	0·0127	0·0254	0·76	1·14
0·0185	0·0185	0·59	0·59	0·0102	0·0102	0·30	0·30
0·0011	0·0011	0·04	0·04	—	—	—	—
0·2704	0·2704	8·60	8·60	0·5584	0·5584	16·65	16·65
—	—	—	—	0·0091	0·0091	0·27	0·27
0·0113	0·0226	0·72	0·36	0·0219	0·0438	1·31	0·66
—	—	—	—	0·0008	0·0016	0·05	0·03
oxygen atoms...	...	...	90·99				88·09

spection of tables III and IV shows that the number of oxygen as to the unit cell of kornerupine is constant within the limits of rimental error, but that the number of metal atoms varies. It is not possible to deduce a general formula for the series which is d on the grouping together of structurally equivalent atoms. A

satisfactory formula can, however, be computed on a purely chemic basis. This can be written as $(R''_2, R''_3, R'_6)_3(Si_3,B_4)O_{15}$.

TABLE IV. Unit-cell contents on basis of 90(O).

	Port Shepstone.			Itrongay.		
Si	15·5	15·5	16	15·7	15·7	16
B	3·2	0·5, 2·7	25	3·1	0·3, 2·8	25
Al	25·3	22·3, 3·0		22·8	22·2, 0·6	
Fe'''	4·6	4·6	17·4	0·8	0·8	20·3
Fe''	0·6	0·6		0·3	0·3	
Mg	8·5	8·5		17·0	17·0	
Ca	—	—		0·3	0·3	
Na	0·7	0·7		1·3	1·3	
Total	58·4			61·3		

TABLE V. Molecular proportions of kornerupine.

	Port Shepstone.		Itrongay.	
SiO_2	4915	$(Si_3,B_4)O_6 = 189$	5177	$(Si_3$, &c.$)O_6 = 19$
B_2O_3	502·6		515·5	
Al_2O_3	4017	$(Al_6,Mg_9$, &c.$)O_9 = 192$	3746	$(Al_6$, &c.$)O_9 = 19$
Fe_2O_3	730·2		126·5	
FeO	185·1		101·6	
MnO	11·3		—	
MgO	2704		5584	
CaO	—		90·95	
Na_2O	112·9		219·4	
K_2O	—		8·49	

In the case of the analysis by van der Walt the TiO_2 was calculat as ilmenite and the P_2O_5 disregarded.

A calculation of the unit-cell contents in terms of the above gro yielded a satisfactory approximation to the whole number 6, the actu figures obtained being 6·1 and 5·9 for the Port Shepstone and Itrong minerals respectively. The unit cell would thus contain 90 oxygen atom Particular formulae were deduced from the general formula as follow

Port Shepstone ... ... $Al_{25}Fe'''_5Mg_8Fe''Si_{15}B_4O_{90}$.
Itrongay ... ... $Al_{23}Fe'''Mg_{17}Na_2Si_{15}B_4O_{90}$.

New analyses of kornerupine from Waldheim and Fiskernæs would of great use in determining the full range of the kornerupine series. T prismatine from Waldheim alone apparently varies considerably composition, and it would be worth while making a fractional separati of the cleaned material in heavy liquids and determining the optic and chemical properties of fractions differing by say 0·005 in speci gravity.

icroscopic characters of the rock.—In thin section under the micro- e quartz, biotite, and tourmaline can be seen to be interstitial to erupine (figs. 1 and 2). These minerals usually show no tendency rd crystal form, especially the tourmaline which is frequently nt in vein- and net-like structures. On the other hand, kornerupine uently shows good crystal outlines. Grandidierite is present as light

Fig. 1.

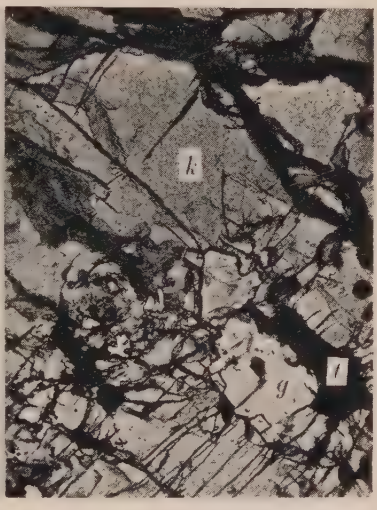


Fig. 2.

. 1. Kornerupine (*k*) showing crystal outlines; with quartz (*q*) and biotite (*b*).

. 2. Kornerupine (*k*) with grandidierite (*g*) and tourmaline (*t*). ×22.

h, pleochroic patches and blebs enclosed in kornerupine. It has, ver, been possible to obtain rod-like crystals of this mineral suitable measurement on the goniometer. Ilmenite occurs disseminated ghout the rock as small, rounded or irregular blebs. In addition ese minerals and small amounts of alteration products (chiefly iron s and a fine-grained mineral resembling sericite), very small nts of graphite and garnet are also present.

e following properties were determined for the minerals:

urmaline.—ω 1·659($\pm$0·004). Pleochroism, ω deep red-brown, t straw-yellow. The refractive indices indicate that the mineral is osed of nearly equal parts of dravite and schorlite.

otite.—β 1·635($\pm$0·004), 2Vα 14°($\pm$2°). Pleochroism, α light yellow, γ dark reddish-brown.

Grandidierite.—α 1·597, β 1·630, γ 1·632 (all $\pm$0·004). Cleavages, *a*(10
b(010). Pleochroism, α light greenish-blue, β colourless, γ light greeni
blue. $\alpha = a$, $\gamma = b$. $2V\alpha$ 29°($\pm$3°), $r < v$ strong. A qualitative chemi
analysis showed the mineral to be chiefly a boro-silicate of aluminiu
and iron.

Garnet.—*n* 1·804($\pm$0·004).

Summary.—Kornerupine, which differs from previously describ
material chiefly in having a higher ferric iron and lower magne
content, is found in the Port Shepstone district, Union of South Afri
An analysis of this material shows that the composition of kornerupi
varies between wider limits than hitherto known. From this and oth
analyses the general formula is deduced as $(R''_2,R''_3,R'_6)_3(Si_3,B_4)O_{15}$.

maucherite (*nickel-speiss*, *placodine*, *temiskamite*).

(With Plate XXIV.)

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[Read March 7, 1940.]

ICKEL-SPEISS (Nickelspeise), an impure arsenide of nickel obtained as a by-product in the manufacture of smalt, has long known as a source of distinct crystals representing a definite cal compound. Such crystals were already analysed by Döbe- (1823), who concluded that the material was an artificial form of lite, NiAs. Later analyses showed that the composition of the llized furnace product approaches Ni_3As_2, a compound unknown ure at that time.

ubstance corresponding to the crystallized nickel-speiss, but thought of natural origin, was first described by Breithaupt (1841), who the material *Plakodin* (πλᾰκώδης, broad) in allusion to the tabular of the crystals. These were said to have occurred in the Jungfer at Müsen in Westphalia, associated with chalybite and gersdorffite o have been salved by a smalt-works official from a shipment of Breithaupt stated that he possessed no attached crystals and was ore obliged to rely wholly on the foregoing information regarding rigin of the material. Since nothing resembling placodine was quently found at the Jungfer mine, and the properties of the ial agreed with those of the known smalt-works product, Breit- 's species became discredited and identified with crystallized -speiss.

ntually this nickel arsenide was found as an undoubted mineral, ated with niccolite, chloanthite, bismuth, manganite, calcite, e, anhydrite, and gypsum, at Eisleben in Thuringia, and named herit by Grünling (1913), after W. Maucher, who had detected the naterial. The material was crystallized as rectangular tablets; its osition was found to be close to Ni_3As_2.

Almost simultaneously, Walker (1914) described a new nickel arsen which occurred in important amounts in the form of rounded masses radiated fibrous structure in calcite at the Moose Horn mine, Elk La Temiskaming district, Ontario. An analysis of this material, nam temiskamite by Walker, yielded the composition Ni_4As_3.

Since the physical properties given for temiskamite are similar those of maucherite and the chemical formulae ascribed to the t minerals are not very different, it has been suggested that the t substances are identical. Indirect evidence bearing on the chemi identity of the two materials was given by Palmer (1914), who deduc the formula Ni_4As_3 for both minerals from experiments involving t precipitation of silver by the nickel arsenides from an aqueous so tion of silver sulphate. Orcel (1928) confirmed the physical identity the two minerals in polished sections, but recommended the chemi formula Ni_3As_2 as the more probable composition. Since the origi analyses of maucherite are inadequate and further analyses have n been made, it cannot be said that maucherite and temiskamite ha been definitely identified or that either of the proposed compositi has been confirmed.[1]

Material and Acknowledgements.

The suggestion that further work on maucherite and temiskam might decide the uncertainties mentioned above came independen from Prof. A. L. Parsons (University of Toronto) and Dr. H. Bern (Harvard University). For the purpose of this work the follow materials were assembled:

1. Maucherite (Royal Ontario Museum of Mineralogy), Eisleben, Thurin Germany (type locality). Three specimens, 1½–5½ inches, of the nearly pure mas mineral with attached baryte and carbonates. On some unbroken surfaces maucherite occurs as meshworks of minute tabular crystals. These specim provided single crystals for X-ray measurements and nearly pure material fo analysis.

2. Maucherite, Sudbury, Ontario. A slab of nearly pure material, 1½ inches, some clean fragments, picked from the concentrator. Similar material was u for an analysis.

3. Maucherite (Harvard Mineralogical Museum), 2600-foot level, Frood m Sudbury, Ontario. Two specimens, 2–3 inches, of massive material associated w pyrrhotine, chalcopyrite, pentlandite, and gangue.

4. Maucherite (Harvard Mineralogical Museum), Orford, Quebec. Mi imperfect crystals which had been separated from an association of chrome-gar

[1] For further details of previous work on nickel-speiss and placodine see Hi (1904, p. 621); on maucherite and temiskamite see Hintze (1938, p. 347).

ene, calcite, and millerite. These crystals had been doubtfully referred to elsbergite ($NiAs_2$) by Palache and Wood (1904) before maucherite was known. Temiskamite (Royal Ontario Museum of Mineralogy). Moose Horn mine, Elk Temiskaming district, Ontario (type material). Several fine specimens, 1–5 , showing the characteristic rosettes with radiated fibrous structure, asso- with niccolite and calcite.

ecimens 1 and 5 were kindly placed at my disposal by Prof. A. L. ons; specimen 2 by Dr. Harcourt of the International Nickel Com- , Copper Cliff, Ontario; and specimens 3 and 4 by Prof. C. Palache. . A. Harcourt also took an important part in the work, particu- in contributing the descriptions of the polished sections. Mr. C. E. ner, now with the Company, assisted in working out the powder graphs. Dr. H. Berman kindly made a series of density measure- s on his specially adapted micro-balance (1939).

Physical Properties.

freshly broken surfaces maucherite and temiskamite are platinum- with a faint but distinct reddish hue and a bright metallic lustre. olour is easily distinguished from the pure tin-white of rammels- e and the pale copper-red of niccolite. Exposed surfaces are often y-yellow to dull coppery-red and consequently the tarnished ial tends to resemble niccolite. The fracture is irregular, controlled e state of aggregation, which ranges from granular to radial- s. No cleavage was obtained from single crystals.

asurements of specific gravity are assembled in table I, which ts the value calculated from the structural cell, published mea- values, and new measurements on small selected fragments. The ted values show a satisfactory consistency, confirming the older

I. Maucherite (placodine, temiskamite): measured and calculated density.

Locality.	Density.	Weight of sample.	Observer.
—	8·04	—	Calculated
Artificial?	8·062	—	Breithaupt (1841)
(placodine)	7·988	—	Breithaupt (1841)
Sudbury	8·00	12·66 mg.	Berman
(maucherite)	7·89	16·57 mg.	Berman
Elk Lake	7.95	28·36 mg.	Berman
(temiskamite)	7·92	28·34 mg.	Berman
	7·901	—	Walker (1914)
Eisleben	7·83	—	Prantl, in Grünling (1913)
(maucherite)	7·77*	10·53 mg.	Berman

* Contained some visible intergrown carbonate gangue.

measurements and showing that there is no significant difference in t specific gravities of the materials named placodine, maucherite, a temiskamite.

Polished sections from materials nos. 1, 2, 3, 5, were examined w a view to verifying the specific properties given in the literature a ascertaining the degree of purity of the materials to be used for chemi analyses. In all the sections the maucherite or temiskamite is pinki grey, similar to cobaltite, and weakly but distinctly anisotropic. T polarization colours are dark grey to light grey. Numerous grains sh twinning. The Talmage hardness, estimated with a steel needle, is The etch reactions are as follows: HNO_3, effervesces instantly a stains black; HCl, negative; KCN, negative; $FeCl_3$, slowly stains brow bringing out the grain boundaries; KOH, negative; $HgCl_2$, slowly sta brown.

In a section from the Eisleben material (no. 1) the ore mine consists almost wholly of maucherite with less than 1% of niccol which encloses white, anisotropic grains (0·1 mm. in diameter) o soft bismuth-bearing mineral amounting to about 1%. The Sudbu material (no. 2) showed up to about 5% of chalcopyrite and 2% silicates. In the Sudbury specimens (no. 3) the maucherite is associat with about 10–15% of pyrrhotine, 3–4% of chalcopyrite, and 1% pentlandite. In the Elk Lake temiskamite (no. 5) etching with HN brings out fine hair-like stringers of a white mineral intergrown with t fibrous temiskamite and unaffected by the acid; $FeCl_3$ reveals the sa structure.

These observations agree substantially with recent standard descr tions (Schneiderhöhn and Ramdohr, 1931, p. 227; Short, 1934, p. 2 confirming the anisotropism which was definitely noted by Orcel (19 but rarely observed by Schneiderhöhn and Ramdohr. As stated Orcel, maucherite and temiskamite are alike in the specific propert observable in polished sections.

Chemical Composition.

Samples of the materials from Eisleben (no. 1) and Sudbury (no. were analysed for comparison with previous analyses of maucherite a temiskamite.[1] As shown in table II the new analyses (I, III) clos

[1] These analyses presented unexpected difficulties. It was found that the c stituents other than arsenic could be reliably determined only after arsenic h been completely removed by prolonged distillation.

ble the old ones (II, IV, V) in their main constituents. Cobalt and ll amount of sulphur appear to enter the composition of the al; the remaining reported constituents may be referred to the ed associated minerals. A discussion of these analyses will be in connexion with the determination of the atomic content of the ural cell.

TABLE II. Maucherite and temiskamite: chemical analyses.

	I.	II.	III.	IV.	V.
Ni	49·96	49·07	50·03	49·51	52·71
Co	0·20	1·73	0·84	0·93	2·15
Fe	0·84	—	trace	—	0·40
Cu	0·69	—	0·13	—	—
Pb	—	—	—	—	0·20
As	45·88	46·34	45·90	45·66	43·67
S	0·97	1·03	0·18	—	0·17
Bi	—	0·55	—		—
H_2O ...	0·36	—	—	—	—
Gangue ...	0·32	—	1·66	—	0·40
	99·22	98·72	98·74	(96·10)	99·70

Maucherite, Sudbury, Ontario; analyst, International Nickel Company.
Temiskamite, Moose Horn mine, Elk Lake, Ontario; analyst, Walker (1914).
Maucherite, Eisleben, Thuringia, Germany; analyst, International Nickel Company.
Maucherite, Eisleben; analyst, Friedrich (in Grünling, 1913).
Maucherite, Eisleben; analyst, Prantl (in Grünling, 1913).

Geometrical crystallography.

rding to previous descriptions crystals of maucherite and the onding artificial material are tetragonal or pseudo-tetragonal, g in habit from tabular (001) to bipyramidal (*hhl*). The basal are sometimes of good quality; the pyramidal planes are always r less striated parallel to the base.

ficial crystals (nickel-speiss) were described by Rose (1833), who combinations of tetragonal bipyramids (*hhl*) with the basal id (001). Breithaupt (1841) interpreted his tabular crystals of ine as monoclinic (pseudo-tetragonal) with a broad side pinakoid d by forms (*hk*0) and (0*kl*). Braun (1879) reverted to the tetra- interpretation of placodine. Rosati (1914) confirmed the tetra- character of placodine and natural maucherite from Eisleben and d that the two materials are substantially alike in crystal form and al composition. Goldschmidt (1920, p. 13) gave a correlation of escriptions, adopting the tetragonal notation of Braun and Rosati. e our crystals of maucherite appear to be poorer than the best

that have been measured in the past it will be useful first to consider
results obtained by Rosati, whose work supersedes the earlier obser
tions. With reference to tetragonal elements his axial ratios are:

$a:c = 1:1{\cdot}0780$ (maucherite)
$1:1{\cdot}1185$ (placodine).

Before the X-ray measurements were undertaken an attempt
made to find the crystal lattice from Rosati's form list (table III).
simplest indices, and the nearest approach to a normal harmo
arithmetic series (Peacock, 1937), were obtained by assigning the indi
(102) to the plane (111) of the old notation. The geometrical lattice t
obtained was found to correspond to the preferred structural latt
The reversible transformation formulae are:

Rosati to Peacock: $(\frac{1}{4}\frac{1}{4}0)/(\bar{\frac{1}{4}}\frac{1}{4}0)/(001)$
Peacock to Rosati: $(2\bar{2}0)/(220)/(001)$

TABLE III. Maucherite and placodine: forms and angles.

Tetragonal; $a:c = 1:3{\cdot}190$.

Forms.		ρ (measured) Rosati.				ρ (calc
Peacock.	Rosati.	Maucherite.		Placodine.		Peacoc
c(001)	c(001)	—	(4)	—	(6)	0°00
t(103)	t(223)	46°47′	(1)	46°24′—46°52′	(4)	46 45
p(205)	p(445)	—	(–)	51 45—51 54	(2)	51 55
o(102)	o(111)	—	(–)	57 07—58 54	(21)	57 55
?(508)	d(554)	—	(–)	62 42	(1)	63 22
v(203)	v(443)	64 12—65°14′	(2)	64 03—65 00	(4)	64 49
?(506)	e(553)	—	(–)	69 52	(1)	69 23
l(101)	l(221)	72 35	(1)	72 54	(2)	72 35
g(504)	g(552)	74 24—75 34	(3)	74 32—74 56	(4)	75 55
h(302)	h(331)	77 12—78 01	(10)	77 48	(1)	78 12
k(201)	b(441)	81 00—81 30	(2)	80 46—81 18	(3)	81 05
q(301)	q(661)	82 56—84 15	(2)	—	(–)	84 02

The figures in brackets give the number of times each form was observed
Rosati on maucherite and placodine. The forms x(11.11.12) and i(887), noted
placodine by Braun but not confirmed by Rosati, are neglected.

Table III shows the two sets of form symbols and Rosati's rang
measurements compared to the angles calculated from the structu
axial ratio. Only d and e, each noted only once on placodine, with p
agreement between the calculated and measured angles, have somew
complex symbols in the new notation. The calculated angles, ρ = (00
($h0l$), lie for the most part within the measured range. Rosati's tra
formed elements compare with the structural ratio as follows:

$a:c = 1:3{\cdot}049$ (maucherite, Rosati)
$1:3{\cdot}164$ (placodine, Rosati)
$1:3{\cdot}190$ (maucherite, Peacock).

w of the striated condition of the crystals the structural ratio is in ase considered to be more reliable than the geometrical ratios. e observed forms of maucherite and placodine all lie in one zone. cting the forms (508) and (506), which may be considered doubtful, rojection points in the zone have the following gnomonic distances om the pole (001):

	c	*t*	*p*	*o*	*v*	*l*	*g*	*h*	*k*	*q*
	(001)	(103)	(205)	(102)	(203)	(101)	(504)	(302)	(201)	(301)
...	0	$\frac{1}{3}$		$\frac{1}{2}$		1	—		2	3
...	0		$\frac{2}{5}$	$(\frac{2}{4})$	$\frac{2}{3}$	$(\frac{2}{2})$	—	$\frac{3}{2}$		

ept for *g*(504) all the points in the zone lie in the primary (*p*) and lary (*s*) harmonic-arithmetic series (Peacock, 1937) which follow usly from the classical law of Bravais as applied to a simple lattice. lowing Donnay and Harker (1937) and Donnay (1938), who alized the law of Bravais by showing the relation between form tance and lattice-plane spacing as given by indices conforming to ace-group conditions, we may obtain further information from ne: (1) lack of systematically weak or absent forms (*h*0*l*) indicates f extinctions in (*h*0*l*); (2) the absence of (100) as a form suggests he indices are (200), as required by a screw-axis 2_1; (3) since the (001) is not always dominant, although $a:c = 1:3{\cdot}190$, the indices e (002) or (004), resulting from screw-axes 4_2 or $4_{1,3}$. Actually the extinctions confirm (1), (2), and the second alternative of (3).

zone (*h*0*l*) offers, however, an alternative choice of lattice, namely as (101) giving $a:c = 1:6{\cdot}380$. The zone series then reads:

	c	*t*	*p*	*o*	*v*	*l*	*g*	*h*	*k*	*q*
	(001)	(106)	(105)	(104)	(103)	(102)	(508)	(304)	(101)	(302)
...	0	$\frac{1}{6}$	$\frac{1}{5}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	—	—	1	—

en terms lie in the primary series, three in higher series. Again the form (100) indicates the indices (200), while the base is probably n view of the axial ratio. This lattice corresponds to a well-marked -cell shown by the X-ray photographs; but the general extinction ion for the pseudo-cell, $(h+k+l)$ even, does not show in the zone

It is remarkable that the morphology should offer two choices of l lattice, both of which are revealed by the X-ray photographs. material available for the present study adds little to the fore- account of the morphology of maucherite. The crystals on one en from Eisleben are minute basal tablets with rectangular or outlines. The base gives a fair reflection permitting polar adjust- on the two-circle goniometer. The striated edge faces give trains

of feeble signals without reliable single reflections. These trains sh
however, that the edges of the tablets are strictly rectangular.

The crystals from Orford, which had been doubtfully referred
rammelsbergite by Palache and Wood (1904, p. 358), gave an X-
powder photograph identical with that of maucherite from Eisleb
These crystals were described as minute and deeply striated, not p
mitting satisfactory measurements. They yielded a provisional ort
rhombic axial ratio:

$$a:b:c = 0{\cdot}5722:1:1{\cdot}1545$$

Approximate correspondence with the lattice of maucherite is
tained with the following correspondence of planes:

Palache and Wood.	Peacock.
(010)	(001)
(014)	(101)
(210)	(011)

The reversible transformations are:

Palache and Wood to Peacock: $(00\frac{1}{4})/(\frac{1}{2}00)/(010)$
Peacock to Palache and Wood: (020)/(001)/(400)

Thus transformed the elements of Palache and Wood give pseu
tetragonal values roughly similar to those of maucherite:

$a:b:c = 1{\cdot}009:1:3{\cdot}495$ Palache and Wood
$a:a:c = \quad 1:1:3{\cdot}190$ Peacock

The form symbols[1] correspond as follows:

Palache and Wood	(010)	(120)	(110)	(210)	(014)	(013)	(012)	(021)	(
Peacock	c(001)	–(014)	o(012)	l(011)	l(101)	–(304)	o(102)	–(108)	–(

Five of Palache and Wood's forms thus correspond to known fo
of maucherite; the remaining four are new, but they cannot be regar
as established, since the material did not yield reliable measureme

A few of the Orford crystals were examined in the hope of obtai
better measurements. In the new setting they have the appearanc
tetragonal bipyramids combined with the base. The striations
general imperfection of the crystals do not permit good measureme
However, 17 reflections were noted on pyramidal planes, with a ra
ρ = (001):($h0l$) = 70° 15′–74° 40′. Some of the best of these g
72° 27′, 72° 29′, 72° 30′, 72° 30′, 72° 30′, 72° 43′, average 72° 3
calculated for l(101), ρ = 72° 35½′. The crystals are thus essenti
combinations of c(001) and l(101), with other weak forms ($h0l$)

[1] Correction: In Palache and Wood (1904, p. 359; 1905, p. 18), *for* ∞2 120
2∞ 210, and vice versa.

. for better material might lead to a more exact description Orford crystals, which represent the only known occurrence of ctly crystallized maucherite in Canada.

Orford material presents a feature which has evidently been noted , namely a lack of strict equivalence in adjoining zones of pyra- planes, [100] and [010]. The plane (011) may be large and bright (101) is narrow and dull; the axes [100] and [010] appear to be axes. This symmetry is in keeping with Breithaupt's monoclinic ption (with $\beta = 90°$) and with Palache and Wood's orthorhombic ient. It is also indicated in Braun's drawing of a placodine crystal p. 423) which shows unlike forms in adjacent zones. On the other it is not possible to interpret the X-ray effects on a crystal from en with reference to symmetry lower than tetragonal. An ex- ion may lie in the fact that maucherite apparently has a defect ure as shown later. In some crystals the vacant positions might be natically arranged, leading to a reduction of symmetry.

inning.—On the specimen from Eisleben the crystals of maucherite quently intergrown in a regular manner, two individuals meeting ely in a common edge [010], often with complete interpenetration. ing was also noted in the polished section. From approximate rements Rosati (1914) found two laws: twin-plane (203), common; win-plane (102) (new notation). We are unable to verify these On several twins the angle [100]:[100]′ varied from 54° to 58°, sured on the microscope. The angle (001):(tw.-pl.) is therefore °. The calculated angle (001):(106) is 28° 00′. The quasi-normal which might be considered the twin-plane, is (407), giving the ated angle (001):(407) = 61° 15′ = 90°—28° 45′. This plane lies en (102) with $\rho = 57° 55'$ and (203) with $\rho = 64° 49'$. While these ations indicate that the twin-plane is (106) confirmation of the aw on better material is clearly necessary.

Structural crystallography.

liminary observations on the structure of maucherite and the tory compound Ni_3As_2 were given by Laves (1935), who obtained -crystal diffraction effects indicating a tetragonal structure with , c 21·7 Å, associated with a two-dimensional (diperiodic) super- ure with $a' = 2a = 6{\cdot}9$ Å.[1] The smaller cell was defined by

[1] ese data appear to have been overlooked by the reviewers; the writer found n searching the literature for work on random structures, after he had found g evidence of randomness in a series of photographs on maucherite.

normal sharply resolved spots; the presence of the superstructure w indicated by streaks of continuous diffraction with indices h and determinate with reference to a, l indeterminate. Laves did not co sider the space-group or the cell-content or the details of the structu which required further investigation.

Using squarish tablets of maucherite from Eisleben (material no. and a camera with radius 28·63 mm. the writer made the following X-r photographs with unfiltered copper radiation: rotation about an ed of the tablet [100] or [010]; equi-inclination Weissenberg photograp of the zero, first, and second layer-lines about the same axis; rotati about the normal to the tablet [001]; equi-inclination Weissenb photographs of the zero, first, second, third, and fourth layer-lines abo the same axis. Powder photographs were also made on the materi nos. 1, 2, 4, 5.

These photographs serve to confirm and amplify the preliminar results of Laves. The projections conform to the Laue symmet $4/mmm$, which includes the classes $\bar{4}2m$, $4mm$, 422, $4/m\ 2/m\ 2/m$. Nea all the sharply resolved spots, and all the powder lines, can be index with reference to a tetragonal lattice:

$$a = 3{\cdot}422 \pm 0{\cdot}005,\ c = 21{\cdot}83 \pm 0{\cdot}05\ \text{Å}.$$

The streaks of continuous diffraction appear as intercalated lay lines in the rotation photograph about [100] and intercalated Weiss berg curves in the Weissenberg photographs about the same axis. T streaks may be given integral indices h, k only with $a' = 2a - 6{\cdot}84$ 0·01 Å. In the rotation photograph about [001] the continuous diffr tions show as intercalated row-lines (Bernal curves) with l indetermina in the Weissenberg photographs about [001] the streaks intersect slot of the layer-line screen, appearing as weak rectangular spo visibly different from the normal sharp diffractions. Complete index of the photographs about [001] requires the larger value of the a-peri In view of the fact that the continuous diffractions do occasiona resolve into definite spots which demand the larger a-period, parti larly in the third layer-line of the rotation photograph about [100], prefer to define the lattice of maucherite with the values:

$$a = 6{\cdot}844 \pm 0{\cdot}01;\ c = 21{\cdot}83 \pm 0{\cdot}05\ \text{Å}.;$$
$$a{:}c = 1{:}3{\cdot}190;\ V = 1023\ \text{Å}^3.$$

and to consider the cell with $a/2$ and $V/4$ as a pseudo-cell.

With reference to the elements of the pseudo-cell the sharply resolv spots conform to the conditions:

(hkl) present only with $h+k+l = 2n$
(hhl) „ „ „ $2h+l = 4n$
($hk0$) „ „ „ $h = 2n$ and $k = 2n$
($00l$) „ „ „ $l = 4n$

ese conditions conform to the general extinctions of the space- $I4/amd = D^{19}_{4h}$, with ($00l$) present only with $l = 4n$ as an extra unexplained condition.

the elements of the full cell all the diffraction effects conform to the tions:

(hkl) present in all orders
($hk0$) „ „
($0kl$) „ „
(hhl) present only with $h = 2n$
($h00$) „ „ $h = 2n$
($00l$) „ „ $l = 4n$

ese conditions conform to the general extinctions of the enantio- nic space-groups $P4_12_1$ – D^4_4 and $P4_32_1$ – D^8_4, with (hhl) present with $h = 2n$ as an extra and unexplained condition.

m the foregoing it would appear that the partially random struc- of maucherite is not subject to the normal procedure of finding the -group symmetry from the systematic extinctions; but further deration of this problem will not be given here.

Powder photographs.

ay powder photographs proved indispensable in identifying the rials used in the present work. Identical patterns were obtained maucherite from Eisleben (no. 1), maucherite from Sudbury 2), maucherite (previously named rammelsbergite) from Orford 3), and temiskamite from Elk Lake (no. 5). In view of the useful- of such patterns, especially for opaque minerals, the maucherite n has been completely indexed with reference to the elements of seudo-cell (table IV). As expected, the continuous diffractions, require the elements of the full cell, do not resolve as powder since they are indeterminate in one index, l.

TABLE IV. Maucherite: powder diagram.

Ip.	*s* mm.	*d* (meas.) Å.	(*hkl*).	*Iw.*	*d* (calc.) Å.
w	15·05β	2·72	(008)β	m	2·73
s	16·75	2·70	(008)	s	2·73
w	19·2	2·36	(112)	s	2·36
vw	20·3β	2·02	(116)β	m	2·02
s	22·6	2·02	(116)	s	2·02
vw	23·05	1·979	(019)	s	1·979

TABLE IV (*continued*).

Ip.	*s* mm.	*d* (meas.) Å.	(*hkl*).	*Iw.*	*d.* (calc.) Å.
m	24·15β	1·711	(020)β	m	1·711
w	25·2	1·819	(0.0.12)	s	1·819
s	26·8	1·717	(020)	s	1·711
w	28·5	1·621	(1.1.10)	m	1·621
w	30·85	1·508	(0.1.13)	s	1·508
s	32·3	1·447	(028)	s	1·450
vw	34·55	1·362	(0.0.16)	s	1·364
vw	36·55	1·297	(129)	w	1·294
vw	38·4	1·243	(0.2.12)	m	1·246
m	39·6	1·211	(220)	m	1·210
			(1.2.11)	m	1·212
m	43·0	1·131	(1.2.13)	m	1·131
m	44·35	1·104	(228)	—	1·106
m	45·5	1·081	(1.1.18)	s	1·084
w	46·4	1·065	(0.2.16)	s	1·067
w	47·75	1·042	(136)	s	1·037
vw	51·3	0·988	(0.3.11)	m	0·989
w	52·6	0·970	(1.3.10)	s	0·970
w	54·9	0·942	(0.3.13)	m	0·944
vw	56·25	0·927	(235)	—	0·929
vw	57·4	0·914	(0.1.23)	s	0·916
w	58·4	0·904	(2.2.16)	—	0·905
w	60·05	0·889	(1.3.14)	s	0·889
w	63·8	0·858	(040)	s	0·855
vw	65·35	0·847	(1.3.16)	s	0·848
w	68·6	0·827	(141)	w	0·829
w	70·3	0·817	(048)	s	0·816
w	72·5	0·807	(0.3.19)	s	0·809
w	73·6	0·802	(0.2.24)	s	0·799

The powder photographs were made with unfiltered copper radiation, the nicke of the mineral suppressing most of the β-lines. Camera radius, 28·63 mm. The tabl gives for each powder ring: the estimated relative intensity of the powder ring (*Ip*) the half-distance between the two branches as measured on the films (*s* mm.); th corresponding spacing (*d* meas.) using $s = 0{\cdot}2$ mm. $= \theta°$; the indices of the correspond ing set of lattice planes (*hkl*); the estimated relative intensity of the correspondin Weissenberg spot, if observed (*Iw*); the spacing calculated from the indices (*hkl*) an the elements a 3·422, c 21·83 (*d* calc.). The generally very good agreemen between *d* (meas.) and *d* (calc.) shows that the powder lines are correctly identifie at least in the great majority of cases. The correspondence between *Ip* and *Iw* i not so close, even when the equivalence factor is applied to *Ip*. This is due to th fact that the Weissenberg photographs were all strongly exposed to bring out th weak continuous diffractions; consequently spots marked *s* are all black, concealin any differences of intensity. Where *Iw* is marked with a dash the indices are no in the range of the Weissenberg photographs taken.

Atomic content of the structural cell.

In view of the uncertainty attached to the empirical formula o maucherite and temiskamite it is essential that the cell-contents b

rmined without reference to supposed simple rational proportions. this purpose three analyses are available (analyses I, II, III of e 2) representing materials from Sudbury, Elk Lake, and Eisleben, se physical properties and identical powder photographs have been ribed above.

TABLE V. Maucherite and temiskamite: atomic content of the pseudo-cell.

	I (Sudbury).			II (Elk Lake).			III (Eisleben).			Ideal.	
	A.	B.		A.	B.		A.	B.		A.	B.
...	51·75	10·93	11·02	49·99	10·49	10·86	51·54	10·65	10·85	51·85	11
...	0·21	0·04		1·76	0·37		0·86	0·18		—	—
...	0·24	0·05		—	—		—	—		—	—
...	—	—		—	—		0·13	0·02		—	—
...	47·52	7·86	7·97	47·20	7·76	8·16	47·28	7·66	7·73	48·15	8
...	0·28	0·11		1·05	0·40		0·19	0·07		—	—
	100·00			100·00			100·00			100·00	
....	8·00			7·95			7·83			8·04	

umns I A, II A, III A represent analyses I, II, III of table II reduced to the of 100% after withdrawing the impurities. Columns I B, 2 B, 3 B give the sponding atomic contents of the pseudo-cell (quarter cell) with the volume 4 Å^3. In each case the highest (most probable) measured density has been used, out correction for impurities. Such a correction would be hardly significant in se of I and II; in the case of III, Prantl's value was taken instead of Berman's, was evidently slightly affected by light impurities.

shown in table V the pseudo-cell contains $Ni_{11}As_8$ in which some it takes the place of nickel and some sulphur replaces arsenic. The ortion 11:8 (1·375) lies between the 3:2 (1·5), the proportion pro- ki for maucherite by Grünling (1913) and generally accepted for the icial crystal, and 4:3 (1·333), the proportion derived by Walker 4) for temiskamite. In view of the tetragonal symmetry it is prob- that the content of the pseudo-cell should be written $Ni_{12-1}As_8$ or $_3As_2]-Ni$ indicating a defect structure in which one Ni-position is nt. The content of the full unit cell would then be $Ni_{48-4}As_{32}$ or $i_3As_2]-4Ni$.

is defective cell-content may be related to the partial randomness rangement indicated by the X-ray photographs. Since our photo- hs are almost exactly like those of Laves, who found that the evi- e of randomness was present both in natural and artificial crystals, ould appear that the defective cell-content is characteristic of the ral. Our work points to four vacant positions in the unit cell, a onable number in a structure with tetragonal symmetry; on the r hand, this number might vary in different crystals producing

appreciable variations in the bulk composition of the mineral. In tha case the content of the structural cell would be written less specifical as $Ni_{48-n}As_{32}$ or $16[Ni_3As_2]-Ni_n$.

Summary.

A physical, chemical, and preliminary structural study of maucheri (Grünling, 1913) from Eisleben, Thuringia, and Sudbury, Ontario, an temiskamite (Walker, 1914) from Elk Lake, Ontario, shows that the materials have identical specific properties and therefore represent single mineral species. Previous observations on the artificial crysta and on placodine (Breithaupt, 1841) leave no doubt that these su stances are identical with the natural mineral. While admitting th possibility that Breithaupt described natural material, and giving cred to Walker for his independent discovery of the species, it is proper, an in keeping with the present usage, to retain the name maucherite f this mineral. The new observations lead to the following characteriz tion of maucherite:

Tetragonal; $a:c = 1:3{\cdot}190$ (from X-ray measurements). Form $c(001)$, $t(103)$, $v(203)$, $l(101)$, $g(504)$, $h(302)$, $k(201)$, $q(301)$. Hab tabular (001) to bipyramidal (101); also radial-fibrous and granula Twinning common, on (106)? Structure cell, a $6{\cdot}844 \pm 0{\cdot}01$, c $21{\cdot}83$ $0{\cdot}05$ Å.; contains $Ni_{44}As_{32} = 16[Ni_3As_2]-4Ni$; a well-marked pseud cell has $a' = a/2$, $c' = c$, and contains $Ni_{11}As_8 = 4[Ni_3As_2]-N$ Cleavage not observed. Talmage hardness, E. Specific gravity, 8·((measured on best material), 8·04 (calculated). Fresh surfaces reddi platinum-grey, with bright metallic lustre. Polished sections pinkis grey, weakly anisotropic. Two new chemical analyses are given.

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Explanation of Plate XXIV.

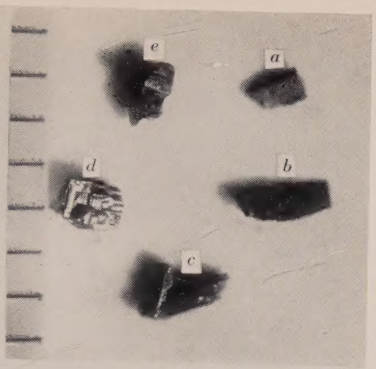
Fig. 1. Maucherite; Eisleben, Thuringia. Nest of elongated tabular crysta with small adhering crystals of niccolite. Scale as in figure 2.

Fig. 2. Maucherite; (*a*) and (*b*), single crystals from Eisleben, flattened on (00 and elongated along [100]; (*c*), twin-crystal from Eisleben; (*d*) an (*e*), imperfect crystals from Orford, Quebec. Scale divisions, 0·5 mm

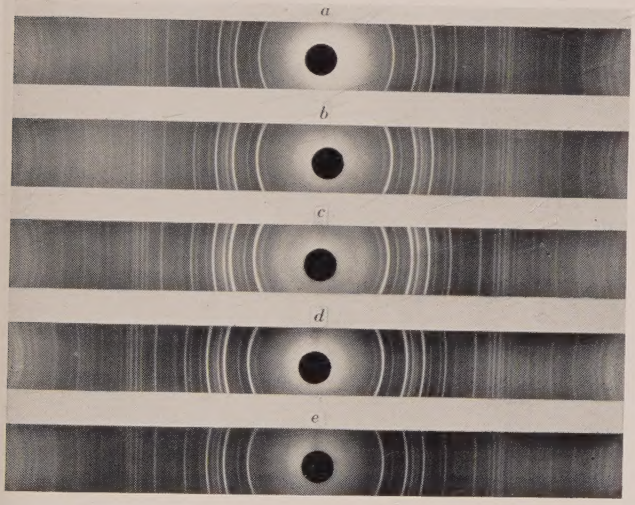
Fig. 3. Maucherite; X-ray powder photographs with unfiltered Cu-*K* radiatio Camera radius, $360/4\pi$ mm. Exposures, 0·3–0·6 KWH. (*a*), Eisleben (*b*), Eisleben ('rammelsbergite'); (*c*), Sudbury, Ontario; (*d*), El Lake, Ontario ('temiskamite'); (*e*), Orford, Quebec ('rammels bergite?').

Fig. 4. Maucherite; crystal lattice. Structural cell in full lines; pseudo-cell i chain-dotted lines; previously used geometrical cell in dotted lines.

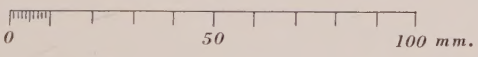
1

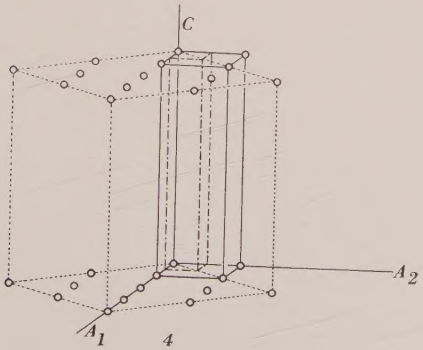


2



3





4

M. A. Peacock: Maucherite.